

**IMPACT OF LAND USE ACTIVITIES ON SEDIMENT-ASSOCIATED
CONTAMINANTS; QUESNEL RIVER BASIN, BRITISH COLUMBIA**

by

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ABSTRACT

The impact of various land use activities (forestry, mining, and agriculture) on the quality of fine-grained sediment ($<63\ \mu\text{m}$) was investigated in the Quesnel River Basin (QRB) (approx. 12,000 km²) in British Columbia, Canada. Samples of fine-grained sediment were collected monthly during the snow-free season in 2008 using time-integrated samplers at sites representative land use activities in the basin. Samples were also collected from replicate control sites, and also from the main stem of the Quesnel River. Results, when compared to Sediment Quality Guideline (SQG) thresholds, suggest that metal mining and forest harvesting are having a greater influence on the concentration of sediment-associated metals and nutrients in the QRB, than agricultural activities. This project contributes to the broader science, and future research in the basin, through a study of multiple land uses in a large basin; a different application of the sediment fingerprinting approach; and a contemporary flume-based sampler evaluation.

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ACRONYMS

A	Agriculture	ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
Ag	Silver	ISQG	Interim Sediment Quality Guidelines
Al	Aluminum	K	Potassium
As	Arsenic	K-W test	Kruskal-Wallis <i>H</i> -test
Ba	Barium	LEL	Lowest Effect Level
Be	Beryllium	Li	Lithium
Bi	Bismuth	M	Mining
C	Control	Mg	Magnesium
Ca	Calcium	Mn	Manganese
CCME	Canadian Council of Ministers of the Environment	Mo	Molybdenum
Cd	Cadmium	M-W test	Mann-Whitney <i>U</i> -test
C/N	Carbon/Nitrogen ratio	Na	Sodium
Co	Cobalt	NAWQA	National Water Quality Assessment
COI	Contaminants of Interest	Ni	Nickel
Cr	Chromium	NO₃⁻	Nitrate
Cu	Copper	OM	Organic Matter
DFA	Discriminant Function Analysis	P	Phosphorus
F	Forestry	Pb	Lead
FAC	Freshwater Ambient Criteria	PEC	Probable Effect Concentration
Fe	Iron	PEL	Probable Effect Level
Hg	Mercury	PPB	Parts per billion
		PPM	Parts per million

PPT	Precipitation
Q	Discharge
QRB	Quesnel River Basin
QRRRC	Quesnel River Research Centre
Sb	Antimony
Se	Selenium
SEL	Severe Effect Level
Si	Silicon
Sn	Tin
SQG	Sediment Quality Guideline
Sr	Strontium
SSA	Specific Surface Area
SSC	Suspended Sediment Concentration
TEC	Threshold Effect Concentration
Ti	Titanium
U	Uranium
UNBC	University of Northern British Columbia
USGS	United States Geological Survey
V	Vanadium
WSC	Water Survey of Canada
Zn	Zinc
Zr	Zirconium

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To Truman, it mostly goes without saying. Thanks for the house that became a home.

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CHAPTER 1: INTRODUCTION

"I understood when I was just a child that without water, everything dies. I didn't understand until much later that no one "owns" water. It might rise on your property, but it just passes through. You can use it, and abuse it, but it is not yours to own. It is part of the global commons, not "property" but part of our life support system."

-- Marq de Villiers

1.0 The aim of this project is to investigate the role of different land use activities on the contaminant concentration of fine-grained sediment collected from the Quesnel River Basin in central British Columbia. This chapter: reviews the relevant literature on this subject; presents the research aims and objectives; and describes the study basin and field sites.

1.1 Literature review

Fine suspended sediments are important in river systems for a variety of reasons including their impacts on aquatic habitats and from a biogeochemical flux perspective (Owens et al., 2005; Syvitski et al., 2005). In addition, most heavy and trace metals can bind to fine-grained sediment, such as suspended material, while in the fluvial environment (Kronvang *et al.*, 2003; Owens *et al.*, 2005; Jha *et al.*, 2007; Walling & Collins, 2005; Horowitz *et al.*, 2008). Contaminant partitioning between dissolved and sediment-binding phases is predominantly controlled by pH (Mouvet & Bourg, 1983), organic matter content (Yin *et al.*, 2002; Gundersen & Steinnes, 2003), and particle size (Förstner & Wittmann, 1983; Horowitz, 1985). Martin & Maybeck (1979) and Audry *et al.* (2004) conclude that it is not uncommon for sediment-associated metals to represent >90% of the metal load in a river. Some metals transported by sediment in rivers have been measured at concentrations 6000 – 10000 times greater than in dissolved form (Luoma & Rainbow, 2008).

Before introducing the objectives of this project it is important to understand better *suspended sediment*; what the term entails, its global scale and distribution, its behaviour within rivers and drainage basins (commonly abbreviated to *basins*), and its

capabilities as a vector of contaminant transport. A broad contemporary definition of sediment, which serves the objectives of this study, is:

Sediment is suspended or deposited individual or composite particles – of mineral and/or organic material, possibly containing water and/or air-filled pores – which has been or is susceptible to being transported by water, wind, ice, mobile organisms, or anthropogenic mechanisms (modified from: Droppo et al., 1998; Solomons & Brils, 2004; Heise, 2007; Owens, 2008).

1.1.1 Global sediment balance

It is estimated that roughly 95% of the sediment entering the global ocean is the result of transfer by rivers from terrestrial sources (Syvitski et al., 2003). The greatest proportional contributions of fluvial sediment into the World's oceans are from mountainous regions with high annual precipitation (Caine, 2004). Syvitski et al. (2003) suggest that this contribution is often greater if the region is prone to tectonic activity and/or land-use induced disturbance such as deforestation.

Sediment fluxes (or loads) are measured in sediment mass transported past a specific location per unit time (Hejduk et al., 2006). The units of measurement are commonly tonnes [of sediment] per year. The term *sediment yield* is similar to sediment flux, but includes the basin area. That is, sediment yield (*specific sediment yield* when referring to annual measurement) is the total amount of sediment that exits a basin, or passes a given point, over a period of time, usually measured in tonnes per year per unit area of the basin (Charlton, 2008).

Figure 1.1 shows that western North America, including a large influence from the combined Columbia and Fraser River basins (including the Quesnel River Basin;

QRB), provide an estimated yield of 131 tonnes per square kilometer per annum ($\text{t km}^{-2} \text{a}^{-1}$) (Milliman, 1990). Southeast continental Asia, the Philippines and Indonesia, which have a Monsoonal climate and orogenous headwaters including the Himalayan Mountains, have the greatest sediment yields, often $>1000 \text{ t km}^{-2} \text{a}^{-1}$.

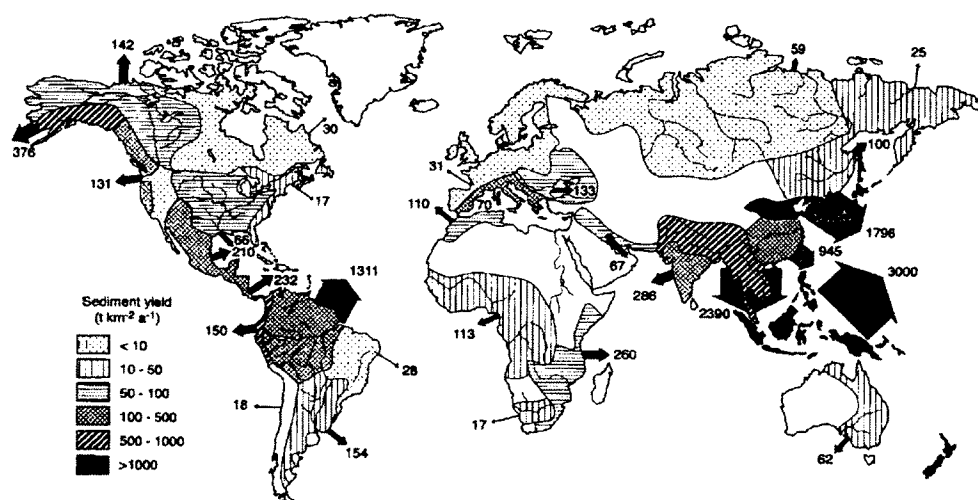


Fig. 1.1 Annual fluvial sediment yields to the oceans from large catchments. Proportion of sediment yield is represented by arrow size. Modified from Dearing & Jones (2003), based on Milliman (1990).

There have been many estimates of mean annual sediment flux from fluvial sources to the global ocean, which range from <10 to $>50 \times 10^9 \text{ t a}^{-1}$ (Panin, 2004; Dedkov & Gusarov, 2006; Walling, 2006). To quantify the impact of human influences on suspended sediment and bedload flux, it is useful to estimate global land to ocean flux during pre-anthropogenic times. Between the late Jurassic and Pliocene sediment input to the global ocean likely represented 2.7 to $5.2 \times 10^9 \text{ t a}^{-1}$ (Panin, 2004). This increased to $15.5 \times 10^9 \text{ t year}^{-1}$ (suspended sediment and bedload values combined) (Syvitski *et al.*, 2005) just prior to the emergence of human beings, representing an entirely *natural* influence. Contemporary studies now estimate the *natural* component of global sediment flux to be $6 \times 10^9 \text{ t year}^{-1}$, while anthropogenic influ-

ences represent $10 \times 10^9 \text{ t year}^{-1}$ (Dedkov & Gusarov, 2006). Thus anthropogenic land use, be it urban, agricultural, deforestation, industrial, or other, has made a marked impact on global sediment flux. Given recent concerns associated with pressures on water resources due to anthropogenic activities (Vörösmarty *et al.*, 2010), the composition and quality (i.e. contaminant concentrations) of this sediment flux is worthy of investigation.

1.1.2 Fluvial sediment behaviour

Material fluxes in rivers can be classified into solid and in-solution forms. Solid, or particulate, material (i.e. sediment) is identified as material being $>0.45 \mu\text{m}$ in diameter, while material $<0.45 \mu\text{m}$ is assumed to be in solution or dissolved (Horowitz, 1991; Walling *et al.*, 2000). At the ultra-fine end of the sediment size spectrum, colloidal material represents particles between $0.001\text{--}1 \mu\text{m}$; thus despite this division between solid and solutional, sediment particles may exist in the “solutional” phase.

Movement of sediment within the channel can be divided into suspended load (median diameter or d_{50} is typically $<2 \text{ mm}$) and bedload (d_{50} typically $>2 \text{ mm}$) transport (Walling & Amos, 1999; Owens *et al.* 2005). It should be noted that this separation, although correct on average, varies from river to river and over time (e.g. coarser load is transported in suspension by higher flows). Sometimes a third distinction of *wash load* is given to sediment that is in perpetual suspension (i.e. is less dense than the surrounding water and is therefore incapable of settling) (Graf & Altinakar, 1998). The suspended size fraction travels within the water column, while the portion of sediment that travels by saltating, sliding, or rolling along or close to the channel bed is classified as bedload. On average, less bedload than suspended

load is transported in most rivers over a year. The ratio of bedload to suspended load is typically in the range 1:5 to 1:50 (Csermak & Rakozki, 1987).

This study is interested in a further classification, which considers all particles $<62.5 \mu\text{m}$ (sometimes rounded to $63 \mu\text{m}$ in the literature) as fine-grained sediment in correspondence with the sand/silt boundary. Although suspended sediment can be as large as 2 mm (d_{50}), a study of several rivers in England and Scotland has suggested that particles $<62.5 \mu\text{m}$ represent 91% to 100% of suspended load (Walling & Moorehead, 1989). Many studies, including this one, have accepted the importance of this grain size division and commonly sieve sediment samples to $<62.5 \mu\text{m}$ prior to analysis (Carter *et al.*, 2003; Horowitz & Stephens, 2008; Walling *et al.*, 2008; Martínez-Carreras *et al.*, 2010).

Traditionally, fluvial sediment particles were conceived as absolute particles (Ongley *et al.*, 1981). That is, discrete grains with the hydro-physical characteristics of a single grain. However, it is now recognized that composite particles (or “flocs”) may make up the predominant form of sediment in the fluvial environment (Droppo & Ongley, 1994; Petticrew & Droppo, 2000), especially if the sediment load is dominated by fine, cohesive material. Since absolute particles refer to single, unassociated grains, whereas composite particles are characterized by structures of multiple particles adhered together, the “effective” particle size of sediment may be several orders of magnitude greater than the “absolute” particle size (Duck, 1984; Droppo *et al.*, 1997, 1998, 2001). Therefore, accurate particle size measurement and conceptualization is important to understanding sediment behaviour (e.g. delivery, transport and storage) in river systems such as the QRB.

Phillips & Walling (1995a; 2005) have reported median effective particle sizes (combination of both composite and discrete particles) of between 5 and 50 μm from rivers in Devon, UK. Studies conducted in southern Ontario, Canada, have recorded median effective particle size values of 14 to 25 μm (Droppo & Ongley, 1994; Droppo *et al.*, 1997; 1998; Petticrew & Droppo, 2000). Although there are differences in the median values of each study, which may be due to differences in collection techniques or hydroclimatic variances, each value lies within the range for fine-grained sediment ($<62.5 \mu\text{m}$).

In some situations, composite particles reliably represent more than 80% of the total volume of sediment in transport (Droppo & Ongley, 1994; Petticrew & Droppo, 2000). Composite particles therefore represent the predominant natural state of sediment within the fluvial environment, eclipsing the long-held stereotype of a discrete particle monopoly (Droppo, 2001).

Two factors control the amount of sediment transported in a basin from source to outlet: (1) the quantity of sediment eroded and delivered to the channel from higher elevations; and (2) a channel's capacity to transport the introduced sediments and to re-mobilize bed and bank materials. Based on the ratio of sediment availability to sediment carrying capacity, rivers are considered as either *supply limited* or *transport-capacity limited*. In general, suspended load is supply limited while bed load is transport-capacity limited (Gordon *et al.*, 1992)

In a river basin there are many mechanisms of sediment transport. Flowing water is recognized as the process with greatest transport capabilities within the river channel, however, there are several processes which may or may not involve flowing water and are capable of significant sediment delivery into rivers (Morgan, 2005;

Charlton, 2008). Mass wasting, in the form of debris flows, rotational slides, rock slides or bank collapse, may provide large sources of gravity-induced sediment input (Church & Slaymaker, 1989; Koppes & Montgomery, 2009). Since such transport may involve the indiscriminant delivery of all material on a given bank or hillslope to the channel, it is a potential source of fine and coarser sediment, including boulders and cobbles. Conversely, Nihlén & Mattsson (1989) and Dahms & Rawlins (1996) suggest that wind may be responsible for mobilization and delivery of predominantly fine sediment from terrestrial sources into rivers. In the QRB, glaciers and snowmelt play a large role in sediment delivery from the headwaters in the Cariboo Mountains.

After introduction into the channel network through the aforementioned processes, sediment can either remain in suspension or go into channel storage. This storage can be short-term (e.g., channel bed and bedforms), longer-term (e.g., behind obstructions), or very long-term (e.g., floodplain deposits) (Megahan, 1982). The quantity and pattern of deposition are predominantly determined by flow velocity and discharge of the river, and the settling velocity and grain size of the material being transported (Simm, 1995).

Flow velocity within the channel can dictate the size of suspended load. Under high-flow conditions, such as storm events or freshets, it is quite possible to suspend material that was previously bed load (Gordon *et al.*, 1992). Concentrations of suspended sediment in fluvial systems may be as low as zero during low or base flow conditions, and $>10 \text{ g L}^{-1}$ during peak flow (Owens, 2008). As mentioned above, high sediment concentrations are often the result of storm events, freshets, and input from mass wasting. However, anthropogenic influences, such as land use changes

may also induce high levels of disturbance and subsequently increase suspended sediment concentrations (SSCs) (Church *et al.*, 1999; Horowitz *et al.*, 2008).

1.1.3 Contaminant transport and flux

In rivers, contaminants are transported in both dissolved and particulate forms. The majority of metals, phosphorus, radionuclides and organic contaminants have a strong affinity with particulates, especially fine sediments $<62.5\ \mu\text{m}$ (Horowitz, 1991; Owens & Walling, 2002). Several studies report that roughly 90% of metals are transported in particulate form (Salomons & Förstner, 1984; Horowitz, 1991; Foster & Charlesworth, 1996). The remaining percentage of metals can be found in dissolved form and are often associated with a combination of low pH in the river waters and metal introduction through industrial practices (e.g., acid mine drainage) (Horowitz, 1985). Partitioning of trace metals and nutrients is a function of environmental conditions (i.e. redox, competitor ions, pH, temperature) and the nature of the contaminant source (Carter *et al.*, 2006; Luoma & Rainbow, 2008).

The number of binding places (or sorption sites) for metals and nutrients on a given sediment particle is determined by grain size (i.e. specific surface area; SSA), and organic matter content (Förstner & Wittman, 1983). Since a sediment load of mainly finer particles has the greatest number of sorption sites (Graf & Altinakar, 1998), grain size is thought to be the most important factor determining sediment-associated contaminant concentrations (Horowitz, 1985). Organic matter, which has been reported to coat the surface of particles (Zuyi *et al.*, 2000), and is an important component of composite particles, may also increase complexity and sorption site quantity (Gundersen & Steinnes, 2003).

In the scope of this study a sediment-associated geochemical element is considered a *contaminant* when it exceeds the lower threshold concentration of nationally and/or internationally recognized sediment quality guidelines (SQG)s. An important consideration is whether the background geochemical element concentration (i.e. control value) is greater than the SQG upper threshold value. In this case, the SQG value still represents the marker for definition as a contaminant since the SQGs are based on the impact of each given geochemical element on organisms. In this scenario, the background geochemical element concentration is considered elevated compared to SQG values and a comment on the position of land use-associated (i.e. forestry, agriculture and mining) geochemical element concentrations compared to the background values can be made. However, the distinction of a geochemical element as a contaminant is still reliant on the associated SQG value.

1.1.4 Effect of land use activities on contaminant and nutrient concentrations

Land use activity is an important factor influencing both the source of sediment and its geochemical and contaminant properties. Horowitz & Stephens (2008) examined the influence of agricultural, forestry, rangeland, and urban land uses on contaminant and nutrient content of fine channel bed sediment. Samples were collected from 51 river basins throughout the USA as part of the National Water Quality Assessment (NAWQA) program of the US Geological Survey (USGS). They found that urban land use had a significant influence on sediment-associated chemical concentrations, while all other land use categories had a lesser effect. Other studies have also demonstrated that land use activities enhance the concentration of sediment-associated contaminants in river systems (for a review see Taylor *et al.*, 2008).

Land uses as contaminant sources may represent one of either point or non-point (diffuse) sources (Jha *et al.*, 2007). Contamination from a point source in a fluvial environment is often expressed as a downstream plume originating at the source and exhibiting abrupt concentration gradients at the plume's perimeter. Diffuse contamination, however, often results in gradual concentration gradients. Possible exceptions to this would be spatially or temporally discontinuous or threshold regulated processes (physical or biochemical) that dictate diffuse contaminant concentration (van der Perk, 2006). Furthermore, whether a contaminant source is point or diffuse is a matter of scale; agricultural land use at the landscape scale can be considered a diffuse source (i.e. a multitude of sources over a large spatial area) but at the level of the individual farm may be a point source (e.g. discharge from farm building or dominant farm drains).

In river catchments there are several commonly observed sediment-associated contaminants for the three land uses sampled in this research project: forestry, agriculture and mining (described below in section 1.2). These contaminants may be divided into the following categories: metals and metalloids (e.g. Ag, As, Cd, Cu, Co, Cr, Hg, Ni, Pb, Sb, Sn, Zn); nutrients (e.g. P, N); organic compounds (e.g. PAHs, PCBs, dioxins, herbicides, hydrocarbons, pesticides); radionuclides (e.g. ^{137}Cs , ^{129}I , ^{239}Pu , ^{230}Th , ^{99}Tc); and xenobiotica and antibiotics (Taylor *et al.*, 2008). The impact of the three land uses that are the focus of this study on contaminant delivery and transport in fluvial environments is described in further detail below.

Forestry, or the mass removal of trees from a landscape through deforestation and the road building and transport of product associated with this practice, is strongly associated with sediment delivery into rivers (Bormann *et al.*, 1974; Hassan

et al., 2005). In the first two years after cutting, an ecosystem will continue to exhibit considerable control over erosion. However, around the two-year threshold, sediment delivery to the river increases exponentially (Bormann *et al.*, 1974). In a best-case scenario, Marks & Bormann (1972) indicate that leaf area indices in a disturbed mature forest can return to previous levels in as little as four years, through natural succession tree growth. However, a full return to old growth stage for the mixed alder-conifer stands and Douglas fir-hemlock-red cedar stands present in the QRB may take 200 yrs. and 500 yrs., respectively (Oliver, 1981).

During and following the two-year sediment delivery hiatus, large woody debris and nitrate (NO_3^-) are mobilized and transported into the fluvial environment. Depending on stream size, large woody debris can drastically alter stream morphology and hydraulics (Hassan *et al.*, 2005). According to Bernhardt *et al.* (2003), NO_3^- loading can lead to increased nitrogen uptake in the stream expressed through increases in algal and aquatic plant production. In extreme cases, such as the 6000% increase in NO_3^- reported in Tremblay *et al.* (2009), the ecosystem may undergo large-scale ecological change such as eutrophication (Carpenter *et al.*, 1998).

Many studies have also demonstrated major changes in element flux cycling in response to forest management practices (e.g. McClurkin *et al.*, 1987; Tiedemann *et al.*, 1988; Johnson *et al.*, 1988; Hendrickson *et al.*, 1989). After a controlled experimental whole-tree harvest by Scott *et al.* (2001), fluvial sediment concentrations of Ni, Cd, Zn, Fe, Sr, Ba, and Mn increased significantly. Heightened geochemical levels persisted for roughly two years. During this period, pH of river water decreased and Cu levels remained constant. In addition to Fe, Tremblay *et al.* (2009) also found increases in K and Mg concentrations in sediments to be associated with deforestation.

A connection has also been made between elevated Zn in sediments in harvested watersheds and culverts used in logging road construction (Christie & Fletcher, 1999).

The impact of agriculture on sediment-associated contaminant delivery to the QRB is closely associated with the agricultural practices in the basin. Grass fields that sustain cattle and other livestock rearing are the predominant agricultural land use. Potential contaminants associated with agriculture include phosphorus (P) (Foy & Lennox, 2006; Collins & McGonigle, 2008) and nitrogen (N) (Wilcock *et al.*, 2009; Panuska *et al.*, 2011), sediment (i.e. from soil erosion), fecal indicator organisms (Tunney *et al.*, 1998), and select metals (Wong *et al.*, 2002; Buccolieri *et al.*, 2010).

Concentrations of P in river waters and sediments are of concern due to connections with stream eutrophication (Parry, 1998), and the propensity of P to be stored and subsequently remobilize in agricultural soil for many years after best management practices have been put in place (Boesch *et al.*, 2001; McDowell *et al.*, 2003).

Metal concentrations in livestock-based agriculture are linked to fertilizers and pesticides or agrochemicals used to enhance grass fields (Kabata-Pendias & Pendias, 1992) and location-specific pollution sources (e.g. atmospheric precipitate of nearby industrial effluent). Commonly enriched metals present in agricultural soils include: Cd, Cu (Wong *et al.*, 2002), Cr, Pb, and Zn (Buccolieri *et al.*, 2010).

The three mining operations studied in the QRB include an open pit copper (Cu) mine, an open hydraulic gold (Ag) mine (inactive but not remediated), and an open pit and underground gold mine. As such, the contaminants of interest are those associated with copper and gold mining. Both metal ores are derived from sulphides, which form in anoxic conditions and, when exposed to oxygen, have the potential

for acid mine drainage (Luoma & Rainbow, 2008). Environmentally significant consequences are associated with acid mine drainage, which can boost leaching of heavy metals from mine tailings and encourage their distribution in the fluvial environment (Protano & Riccobono, 2002). Furthermore, Cu and Au, due to the extraction and concentration processes, will also be present in the waste products (Apte *et al.*, 1995).

In the QRB, the contaminants most likely associated with copper mining include As (Azcue & Nriagu, 1995), Cr (Manahan, 2000), Pb, Mn and Zn (Pestana & Formoso, 2003). Those linked to gold mining practices include As, Cd, Cu, Pb (Azcue *et al.*, 1995), Mn, Zn (Florea *et al.*, 2005) and cyanide (Korte & Coulston, 1998). Luoma & Rainbow (2008) suggests that a combined list for copper and gold mining-associated trace metals may include Sb, Bi, Co, Ge, Mo, Ag, Se, and Te, found in waste products of both processes. Any of the above mentioned elements can enter the fluvial environment, from the mining point source, through processes such as leaks in protective liners and subsequent leaching, and overflow of open piles and solution ponds (Korte & Coulston, 1998).

A main concern in the context of contaminants in fluvial systems is that sediment-associated contaminants will accumulate in small benthic organisms and fish that live in and on the river bed such as mayflies, worms and sturgeon. Then, either through contact with the sediment or consumption of contaminated organisms, the contaminants may transfer through the food chain to other (and most likely larger) aquatic and terrestrial wildlife, including humans (Persaud *et al.*, 1993). Increasingly, higher sediment-associated concentrations of contaminants tend to be amassed by

each successive organism on a foodchain, this process is called biomagnification (Castilhos & Bidone, 2000; Jasonsmith *et al.*, 2008).

1.2 Project overview

This research focuses on the impact of land use activities on fine sediment-associated contaminants in the Quesnel River Basin (QRB), British Columbia, Canada. While several contaminant source and transport studies have been conducted at the broad national scale (e.g. Horowitz & Stephens, 2008), this research project specifically examines the effect of three land use activities (mining, agriculture and forest harvesting) on sediment-associated contaminant (metals and nutrients) concentrations. The study focuses on sampling high-energy events (precipitation events and/or spring freshets) that typically provide the greatest fine sediment and associated contaminant fluxes in river systems. The contaminant properties of the sediment collected from the three different land use types are compared to those collected at two reference (control) sites.

The specific objectives of the project are:

- (1) to determine the contaminant concentrations of fine suspended and channel bed sediments associated with different land use activities;
- (2) to examine if there are temporal and spatial differences between land uses; and
- (3) to determine the QRB-scale suspended sediment signature, through a bottom-up, source ascription, method.

An additional objective is:

- (4) to evaluate the sediment mass and grain size efficiency of the time-integrated sampler used to collect suspended sediment samples.

The sections below outline the study sites and research methodology used to achieve these research objectives.

1.3 The Quesnel River Basin

The QRB (~12 000 km²) (Figure 1.2) is located in south-central British Columbia. It is prime habitat for anadromous salmonids such as sockeye, pink, chinook, and coho salmon and several other non-anadromous species that are important from an ecological and economic perspective. Average total annual precipitation in the basin is 517 mm at the mouth of the river and 1072 mm near its headwaters (Burford *et al.*, 2009). This variation is partially due to elevation change, from ~500 m at the mouth to ~3000 m above mean sea level (a.m.s.l.) in the headwaters. Over half of the basin drains into Quesnel Lake (maximum depth 506 m; Campbell, 2001). From the lake, the river flows ~100 km northwest to the town of Quesnel where it joins the Fraser River (drainage area is approx. 232,000 km²). The headwaters of the Quesnel River are located in the Cariboo Mountains, which provide an orogenous (an area where the process of mountain building has occurred, or is actively occurring) sediment source.

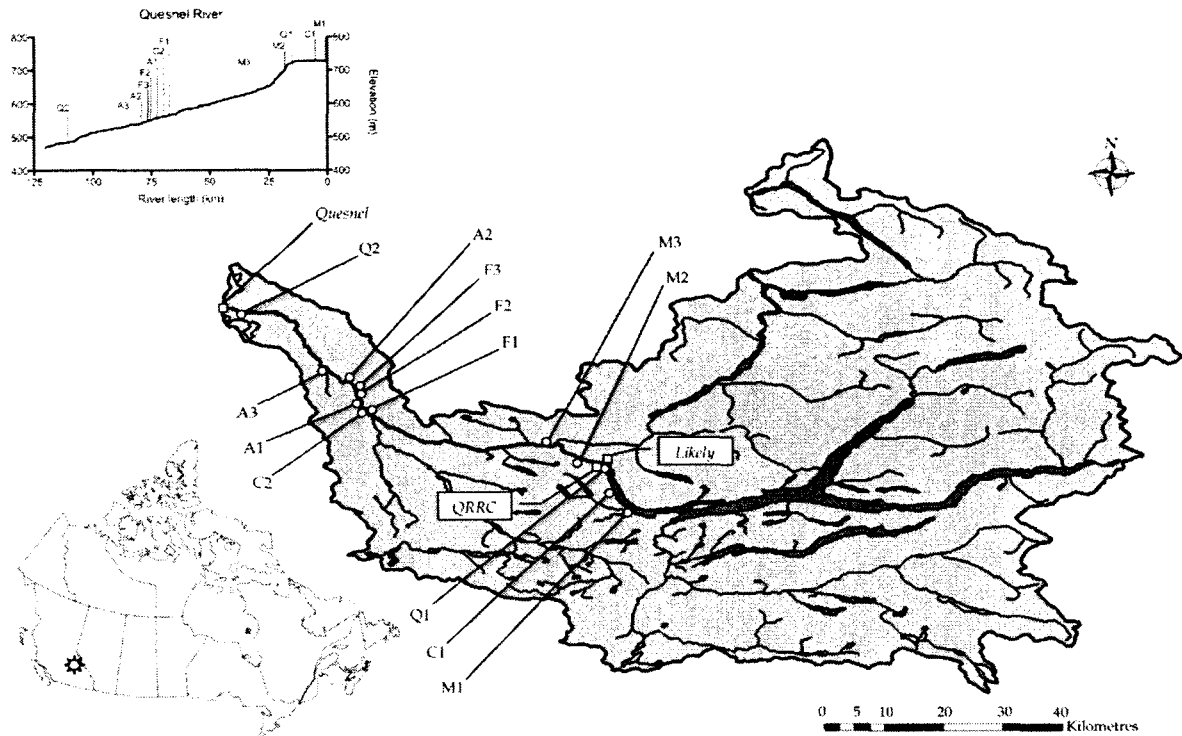


Fig. 1.2 Quesnel River Basin, British Columbia, and location of the sampling sites: F, forestry; A, agriculture; M, mining; C, control; Q, Quesnel River (main channel). QRRC is the Quesnel River Research Centre. The river flows from the Cariboo Mountains in the east to the city of Quesnel in the west, where it joins the Fraser River.

Most of the QRB is frozen for 5–6 months of the year as minimum annual temperatures are typically below -30°C . River flows are dominated by the annual freshet and peak flows occur between late May and early July. Mean discharges for the Quesnel River at the Water Survey of Canada (WSC) gauging stations at Likely ($52^{\circ}37'\text{N}$, $121^{\circ}34'\text{W}$, area is 5930 km^2) and Quesnel ($52^{\circ}50'\text{N}$, $122^{\circ}12'\text{W}$, area is $11,500\text{ km}^2$) were 132 and $248\text{ m}^3\text{ s}^{-1}$, respectively, in 2007 (the last year of available data: WSC, 2009).

The Quesnel basin is influenced by four predominant land use activities (Figure 1.3): (1) forest harvesting; (2) agriculture (mainly livestock); (3) mining (mainly for

copper and gold); and (4) urban, although these are very limited (the population upstream of Quesnel is only a few thousand people), and therefore ignored here.

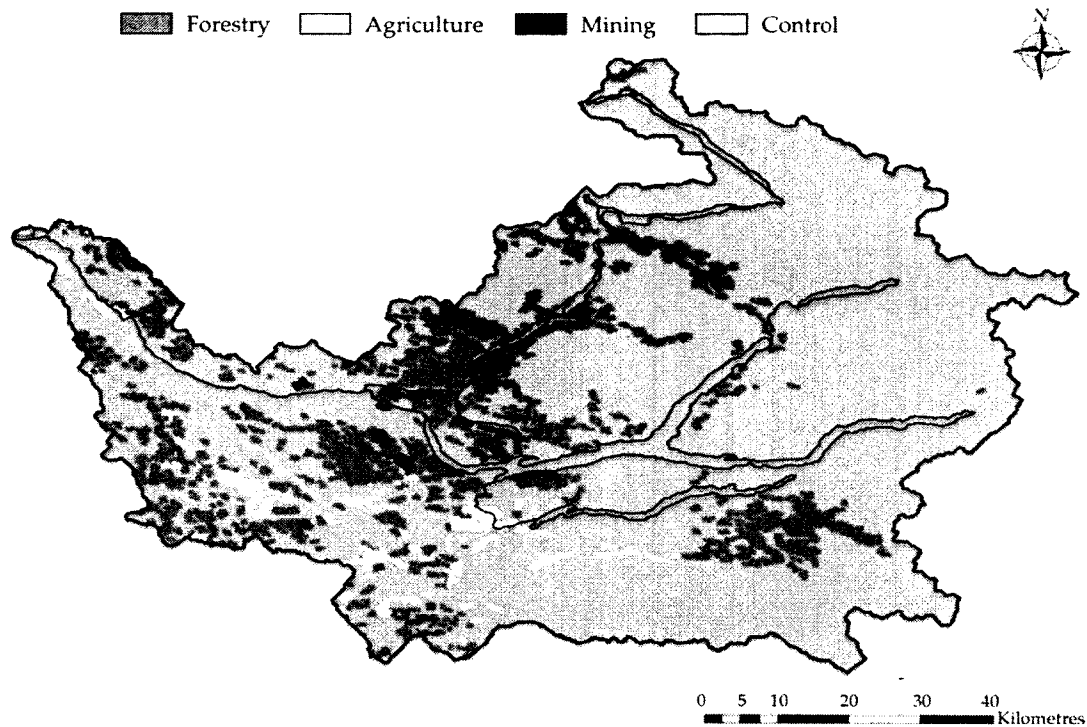


Fig. 1.3 Areal land use distribution in the Quesnel River Basin, British Columbia. Forestry, agriculture, mining and control (e.g. non-harvested forest land) land uses are presented.

In the QRB, in 2008, the areal distribution for each land use was: forestry = 31.9%, agriculture = 5%, mining = 0.3% and control = 62.8%. This project focused mainly on the area of the basin below the output of the lake (located at the community of Likely) as it is assumed that the lake will trap most (>95%) of the inflowing sediment load from the upstream basin.

1.4 Study sites

Suspended sediment samples were collected during the snow-free season in 2008, in stream reaches draining the following land use activities: forest harvesting; agriculture; mining; and reference or control (i.e. relatively unimpacted). Samples were col-

lected at triplicate sites for each land use where the area upstream was dominated (>50%) by a particular land use (e.g. forestry or agriculture) or by an activity likely to influence the sediment quality in the stream (e.g. mining). Triplicate sites were used so to: (i) obtain a more spatially representative measure of land use influences on sediment-associated contaminants; and (ii) assess variations within each land use type and (ii) to assess variation between the three land uses sampled in the QRB.

Unless otherwise referenced, all land use information (e.g. area, slope) for forestry and agriculture in the QRB described below, was retrieved from the Hectares BC website: <http://hectaresbc.ca/app/habc/HaBC.html>. The site is maintained by, and referenced as, Biodiversity BC and the Nature Conservancy of Canada (2012).

Given that 63% of the area of the QRB is forested (Burford *et al.*, 2009) and that significant historical and contemporary forest harvesting has taken place over a large portion of the total area, the impact of forest harvesting practices on suspended sediment geochemistry is worthy of study within the aim of this research project. All forestry sites – F1, F2, and F3 – are in a similar reach of the Quesnel River (Fig. 1.2) and are subject to similar weather, climate, and lithology. The QRB is divided into two forest districts. Quesnel Lake and the southern portion of the basin are within the Central Cariboo Forest District (Government of BC, 2008a), where 1,190 km² were recently logged (i.e. during the last 20 years). The northern portion of the basin including most of the Quesnel River, is in the Quesnel Forest District (Government of BC, 2008b). Here, 189 km² have been recently logged (i.e. within the last 20 years). Sites F1, F2 and F3 are actively logged for sub-boreal spruce and are in the Quesnel Forest District. Hillslopes of logging plots in the study sites are generally

between 3° and 30°. That is, 78% are steeper than 3°, while 99.3% are less steep than 30°.

All three agricultural sites – A1, A2, and A3 – are within the lowland section of the Quesnel River characterized by floodplains and steep exposed cutbanks. The sites represent pasture land, with cattle being the predominant livestock. Site A3, is a hobby farm and contains both Black Angus cattle and horses, while sites A1 and A2 contain beef cattle exclusively. At all three locations there was no barrier between the cattle pastures and the tributaries where samples were collected. Pasture slopes at the study locations, and indeed throughout the QRB, were moderately flat and predominantly less than 15°. That is, 97.4% of agricultural hillslopes in the QRB are <15° and 36.5% are less than 3°.

For mining sites, M1 represents the Mt. Polley open pit copper mine. Since commencing operation in 1997, 7.49×10^7 tonnes of material have been mined and 6.69×10^7 tonnes have been milled. This has resulted in the recovery of 1.96×10^8 kg of copper (Meredith-Jones, 2012). Such practices have typically been associated with the release of Cu and local geology-specific geochemical elements (e.g. Cr), into river systems above background levels (Luoma & Rainbow, 2008). At high concentrations, both chemicals are toxic and Cu in particular is lethal to vegetation (Manahan, 2000). These trace metals are potential contaminant inputs to the QRB from Mt. Polley mine via Hazeltine Creek. While this site discharges to Quesnel Lake via Hazeltine Creek, and is thus upstream of the QRRC and Likely (see Fig. 1.2), it was included here as it is the largest active mine within the basin and its activities are of considerable local concern in terms of the delivery of contaminants to downstream aquatic systems.

Site M2 was the Bullion Pit placer mine, also known as Dancing Bill's Gulch (Figure 1.4). The mine was in operation from 1892 to 1942. In 1935 it was the location of the largest hydraulic monitors (i.e. high-pressure and high-volume water nozzles) ever installed in North America. A network of over 64 km of canals were used to direct water from nearby lakes and creeks to feed the hydraulic nozzles, which used more water each day than the entire city of Vancouver at the time. Currently, the Bullion Pit canyon measures 3 km long by 120 m deep. During operation, it displaced $\sim 2.00 \times 10^8$ tonnes of gravel, along with unknown amounts of sand, silt and clay, recovering 5.46×10^6 g of gold (Flower, 2009).

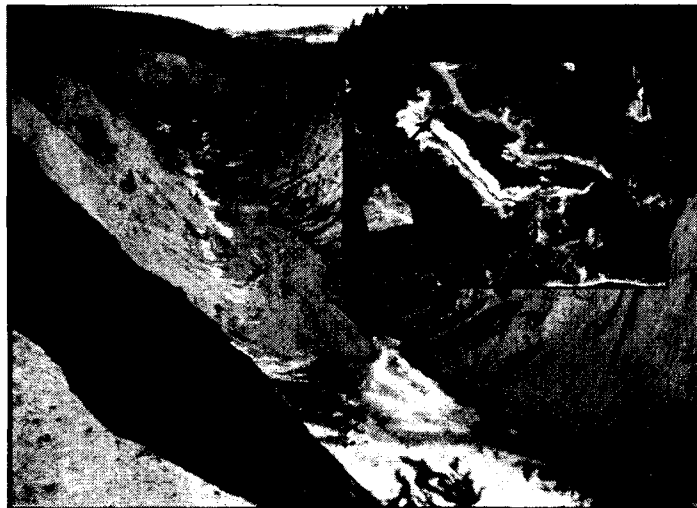


Fig. 1.4 Bullion Pit hydraulic gold mine of site M2. Despite inactivity since 1942, the canyon remains an open scar in the landscape with high sediment delivery potential. Overhead view of site with sampler location is represented in upper right corner.

Site M3 is approximately 8 km downstream of Quesnel Forks, where the Cariboo River meets the Quesnel River. This site is the Cross Lake gold mine, which has both open pit and underground operations. Although fully operational during the field season of this study, Cross Lake Minerals Ltd has (as of December 22nd, 2008) temporarily shut down this mine due to lower than expected ore production and grade.

The reference (or control) sites, C1 and C2, were chosen due to a lack of evidence of recent disturbance within both sub-catchments, suggesting that suspended sediment quality should be indicative of natural boreal forest inputs. However, much of the region has been previously deforested and it cannot be assumed that either site represents an entirely virgin wilderness.

In order to address research objective 3, two sampling sites were located on the main stem of the Quesnel River: Q1 was located at the QRRC and is representative of the outflow of Quesnel Lake; and Q2 was located at the town of Quesnel, and thus is representative of all contributions from the upstream catchment, particularly those downstream of the lake.

1.5 Summary

Water and sediment quality are receiving increasing attention due to the demands placed on freshwater resources and aquatic ecology. This study investigates the impact of contrasting land use activities – active or recent deforestation, agriculture, and mining – on sediment quality in the QRB. This goal was achieved through the following: determination of fine sediment-associated contaminant concentrations linked to each land use; examination of spatial and temporal variation between land uses; and determination of the QRB-scale signature through source ascription-based extrapolation. A secondary objective was to evaluate the time-integrated sampling method used in this project, which has yet to be used in central or northern BC. This research will broaden the scope of information and understanding of sediment-associated geochemical processes in the QRB, and will be useful in the promotion of better river health and stewardship in the region.

CHAPTER 2: EVALUATION OF THE SEDIMENT SAMPLER

2.1 Introduction

The time-integrated suspended sediment sampler described in Phillips *et al.* (2000) (hereafter predominantly referred to as the *Phillips sampler*; Fig. 2.1) has many advantages over previous field techniques to collect representative fine-grained sediment samples (Wren *et al.*, 2000), which include comparatively expensive automatic samplers (Gebhart *et al.*, 1998; Peart, 2003; Eaton *et al.*, 2010) and labour-intensive manual sampling methods (Collins *et al.*, 1998; Jha *et al.*, 2007). Further, it is cost-effective and simplistic in design and construction, and believed to be reliable (Phillips *et al.*, 2000). It can also be deployed indefinitely in the absence of a power source and requires little to no maintenance (Russell *et al.*, 2000). Since its inception in 2000 it has been tested and employed in a variety of fluvial environments in many countries and its use appears to be growing. In order to assess its use in this study (Objective 4), a controlled flume-based evaluation of sampler mass and particle size efficiency was conducted.

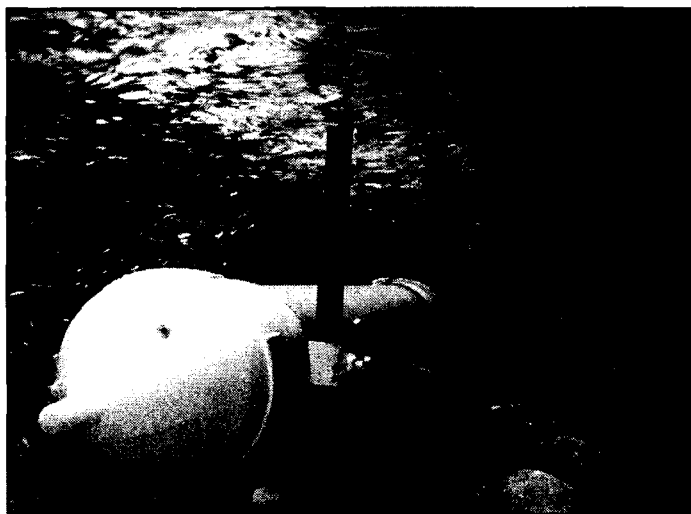


Fig. 2.1 Phillips time-integrated sediment sampler during field deployment (photo courtesy of Phil Owens).

The time-integrated sediment sampler deployed in the QRB in this study, and based on the design specifications of Phillips *et al.* (2000), was tested at the Quesnel River Research Centre (QRRC), near Likely, BC. Using a former salmon-rearing flume, the ability of the Phillips sampler to collect representative samples of suspended sediment – in terms of mass and median grain size (d_{50}) – was assessed in a simulated river environment (i.e. a flume). Comparisons were made between sampler-retained and ambient sediment mass and grain size at the end of each experimental trial.

Additionally, grain size distributions of sediment collected by the Phillips sampler in the field were compared to bed sediment samples collected at the same sites. When sieved to $<62.5\ \mu\text{m}$, the bed sediment samples are plausible surrogates for the ambient suspended sediment load, thus enabling an examination of the grain size efficiency of the Phillips sampler in the natural environment.

As the Phillips *et al.* (2000) study represents the only flume and lab-based calibration of the sampler in the literature it is the primary basis for comparison to the experimental results presented here. Furthermore, the growing deployment of the Phillips sampler in increasingly varied and dynamic applications (e.g. Martinez-Carreras *et al.*, 2010; Panuska *et al.*, 2011) makes a contemporary evaluation of its performance both timely and relevant.

2.1.1 Global sampler deployment

Several studies have been conducted using the Phillips sampler in the U.K. (e.g. Ankers *et al.*, 2003; Evans *et al.*, 2006; Hutchinson & Rothwell, 2008; Walling *et al.*, 2008), Australia (e.g. Laubel *et al.*, 2003), New Zealand (e.g. McDowell & Wilcock,

2007), the United States (e.g. Fox & Papanicolaou, 2007, 2008; Fox, 2009), Japan (e.g. Mizugaki *et al.*, 2008; Fukuyama *et al.*, 2010), France (e.g. Poulenard *et al.*, 2009), and Nunavut, in the Canadian High Arctic (e.g. McDonald *et al.*, 2010). However, it has found limited use in North America and even less in BC. Dr Sandra J. Brown of the University of British Columbia (UBC) is a noticeable exception, having conducted studies using the Phillips sampler in the Lower Fraser Valley and Okanagan basins, BC. This study in the QRB, with the recent exception of McDonald *et al.* (2010), represents one of the northern-most utilization of the samplers in North America to date.

2.1.2 Sampler evaluations

Assessment of the effectiveness of the sampler in the fluvial environment is essential for the interpretation of any sampler-derived data. However, few efficiency tests have been conducted. In the seminal paper by Phillips *et al.* (2000) both flume and field-based evaluations of sampler hydrologic characteristics and sediment mass and grain size efficiency were conducted. Flow velocity in the main cylinder was determined to decrease by a rough factor of 600, in comparison to external flow, due to the cross-sectional area ratio between the inlet tube and the main cylinder. It is this reduction in flow that causes sediment to settle out in the chamber. Using dye and a transparent sampler, internal flow dead-zones were noted adjacent to the inlet and outlet tubes, providing preferential locations for sediment settling (Phillips *et al.*, 2000).

Furthermore, sampler efficiency tests in a controlled environment resulted in a mass retention in the range of 31% to 71%, with greater mass efficiency associated with coarser sediment particles. Coarser median grain sizes were also retained in the

sampler compared to ambient median grain sizes. Phillips *et al.* (2000) found that some of the finest grains remained in suspension while inside the sampler. Thus, some finer sediment passed through the sampler, while all coarser sediment was captured. Besides preferential selection of coarser grains, turbulence in the ambient flow of the flume, although difficult to calculate, was also suspected as a factor reducing sampler efficiency. Indeed, it was determined that flow velocity is reduced in the sampler inlet tube by frictional drag and the inertia of the comparatively stagnant water within the sampler. Thus, water exiting the sampler is slower than ambient flow and the sampler is not isokinetic.

Field-based tests of the sampler were also conducted by Phillips *et al.* (2000), this time testing grain size efficiency and sediment-associated nutrient (total carbon) representation. Both the resulting grain size distributions and nutrient concentrations were statistically representative of ambient conditions.

A second appraisal of the Phillips sampler, conducted during field deployment, was undertaken by Russell *et al.* (2000). Testing determined that the sampler was able to capture a representative time-integrated sample of fluvial suspended sediment. This was determined by analyzing an array of geochemical properties of sampler-collected sediment in comparison to the ambient suspended sediment load of the test river. As in Phillips *et al.* (2000), ambient field-based suspended sediment particle size characteristics were statistically representative of those collected in the sampler.

Importantly, Russell *et al.* (2000) suggested that testing and calibration of the performance of the sampler was required for each new river and/or reach. This point justifies calibration of the sampler for this study and is usually neglected by other

studies citing Russell *et al.* (2000). In other words, researchers tend to cite Phillips *et al.* (2000) and/or Russell *et al.* (2000) as justification for using the sampler without assessing its suitability and representativeness in new locations.

The most recent field evaluation of the Phillips sampler was conducted in Nunavut in the Canadian High Arctic by McDonald *et al.* (2010) at sites characterized by highly variable and episodic hydraulic and sediment transport conditions. Like the Phillips *et al.* (2000) evaluations, the study investigated whether the Phillips sampler could collect a representative sediment load over an extended time period. Sampler efficiency was based on daily-retained suspended sediment mass and median grain size (d_{50}) distribution compared to equivalent values for ambient flow. However, the sampler design was modified from Phillips *et al.* (2000) to adjust for dynamic river stage variations and comparatively smaller channels (peak flow width of 10–15 m). To correct for sediment remaining in suspension and exiting the sampler, the outlet tube was placed at the top of the end cap as opposed to the centre. Most dimensions of the McDonald *et al.* (2010) sampler were smaller than in the original design (e.g. main body 228 vs. 1000 mm in the Phillips *et al.* (2000) version) as dictated by the smaller channels. Two sampler anchorage techniques were used: (1) a fixed-depth apparatus using a boom affixed to the channel bank, as anchorage directly into the frozen riverbed was not ideal; and (2) a variable design using two parallel pivoting aluminum arms to enable automatic maintenance of 60% depth with stage variations (c.f., Eads & Thomas, 1983).

When tested for the mass of sediment captured and its grain size composition, the Phillips sampler proved inefficient, that is, ambient SSC and median grain size (d_{50}) were not proportionate to sampler values. Both over- and under-retention of

sediment compared to anticipated values were recorded. Sediment in both sampler designs displayed significant coarsening compared to ambient flow. However, compared to each other, similar grain size distributions were recorded for both sample designs. Although temporal trends were similar between sediment retention rates and flow velocity, discharge, and SSC fluctuations, retained sediment was significantly coarser and of inconsistent quantity versus ambient values (McDonald *et al.*, 2010).

The authors identified that factors such as organic detritus blocking the inlet tube, the potential of large composite particles, higher velocities than in the Phillips *et al.* (2000) study, smaller trap design (e.g. reduction of sediment capture potential due to a smaller cross-sectional area ratio than in the larger design), were all potential sources of the lower efficiency of mass retained. Perhaps the most important factor identified by McDonald *et al.* (2010) was that the relationship between water intake of the sampler and the modified inlet tube and sampler body diameters had not been examined in the laboratory to properly characterize and quantify hydraulic conditions. Had this been the case, an equation accounting for the frictional and inertial forces acting on the inlet tube could have been used in calculating the anticipated sediment retention of the samplers.

Despite these potential obstacles to full acceptance of the results presented in McDonald *et al.* (2010), the introduction of the automatic variable depth capture method may be an important improvement on sampler anchorage design.

All three sampler evaluations have furthered the understanding of hydraulic characteristics and representative suspended sediment collection efficiency of the Phillips sampler. This chapter provides an additional, independent evaluation of the

Phillips sampler using a flume. Suggestions are then made addressing future sampler design and evaluation improvements.

2.2 Methods

2.2.1 Sampler design

The Phillips sampler is designed to collect samples of actively transported fine-grained suspended sediment in the fluvial environment. The main body of the sampler (Fig. 2.2) is comprised of commercially available polyvinylchloride (PVC) pipe (9.8 cm internal diameter (i.d.) \times 100 cm length) with threaded cap seals at both ends of the cylindrical pipe. Semi-rigid nylon pneumatic tubing (0.4 cm (i.d.) \times 150 mm) provide the inlet and outlet tubes and are threaded through each end cap, and made watertight with silicone sealant. The tubes extend 2 cm into the internal cavity of the sampler at either end. A polyethylene funnel is secured to the upstream end of the sampler and over the inlet tube to provide a more streamlined shape and reduce ambient flow disturbance in the intake tube region. The main body and inlet/outlet tubes have internal (length-ways) cross-sectional areas of 754.3 cm² and 1.26 cm², respectively.

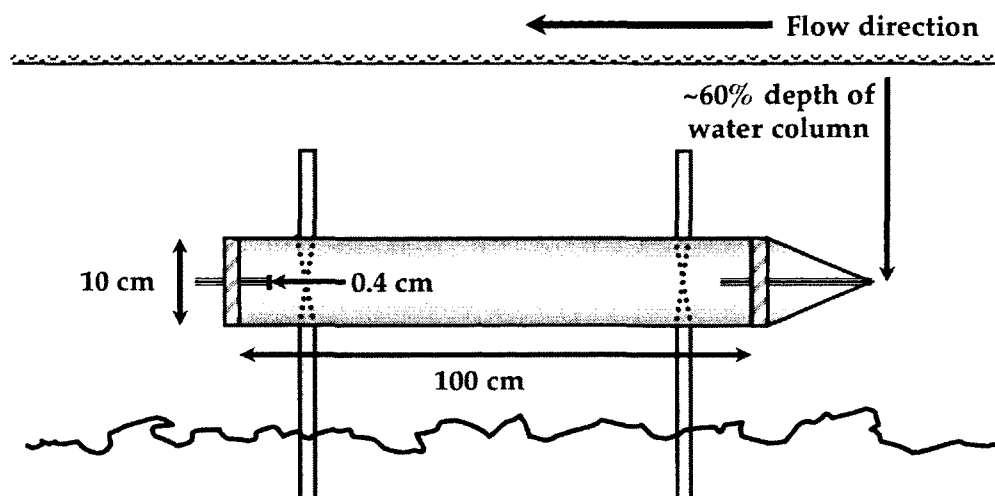


Fig. 2.2 Cross-section of Phillips time-integrated sediment sampler. Flow velocity within the main chamber of the sampler is reduced by a factor of about 600 compared to ambient flow (Phillips *et al.*, 2000; Russell *et al.*, 2000).

This difference in internal cross-sectional area is the crux of the Phillips sampler's operating principle. Water enters and exits the inlet and outlet tubes at a velocity slightly less than ambient flow velocity due to frictional forces in the inlet tube and inertia reduction induced by the comparatively stagnant water in the sampler's main cylinder. To be more precise, the main cylinder of the sampler has an internal cross-sectional area ~600 times larger (598.7x) than that of the inlet/outlet tubes and sampler internal velocity is decreased proportionally (Phillips *et al.*, 2000; McDowell and Wilcock, 2007). Thus sedimentation occurs within the main cylinder.

Some slight modifications to the original Phillips *et al.* (2000) sampler were made prior to fluvial deployment to ensure strong sampler anchorage in the higher flow velocities associated with the Quesnel River and many of its tributaries. As mentioned in section 1.3, the Quesnel River has a mean historical freshet discharge of $350 \text{ m}^3 \text{ s}^{-1}$ with a maximum discharge of over $600 \text{ m}^3 \text{ s}^{-1}$ (WSC, 2010). The peak flow during the 2007 season, which preceded the field season for this study, was $425 \text{ m}^3 \text{ s}^{-1}$. The structural integrity enhancements became increasingly pertinent after above-

average snowfall was experienced within the catchment in the winter of 2008, suggesting a strong spring freshet.

In the Phillips *et al.* (2000) version, metal eyes were screwed into the front and rear of the sampler and used to attach the sampler to steel (Dexion) uprights. In this study, cylindrical hose clamps were attached to the main body of the sampler near the upstream and downstream ends and looped through 4 cm x 4 cm steel cylinders. A hole was drilled in the side of the cylinders and a steel nut was welded onto the hole. This modification allowed a flat-ended bolt to be screwed through the nut and into the steel cylinder to create a fastening mechanism. The cylinders were able to slide over two steel reinforcement bar (rebar) uprights, which anchored the sampler and were sunk into the sediment. The sampler was easily fastened at a chosen depth within the water column and was adjustable during future sampling periods in response to changes in water level. This method of fastening the samplers to the anchorage rebar pieces ensured that there was no unstable movement of the sampler, as with the metal eye method proposed by Phillips *et al.* (2000). For increased stability and trap retention, additional hose clamps may be attached.

2.2.2 Flume-based experimental apparatus

The Phillips sampler was suspended in-situ in a modified Capillano flume at the QRRC. The flume was semi-circular in cross-section, with a diameter of 70 cm and length of 640 cm (Fig. 2.3). The volumes of the flume and Phillips sampler were 1231.5 L and 8.68 L, respectively. An aluminum boom, capable of vertical adjustment, was fastened to the lip of the flume and used to keep the Phillips sampler pointed into the current and at 0.6 of the water depth. In an attempt to reduce the influence of turbulence on sampler efficiency (Phillips *et al.*, 2000), the nose cone of

the sampler was over 1 m from a turbulence-reducing grate, where buffered turbulent flow has been measured in previous flume-based experiments at the QRRC (Rex & Petticrew, 2008). A pump was connected to the drain at the “downstream” end of the flume. This enabled recirculation of the water and sediment and created continuous flow within the flume.

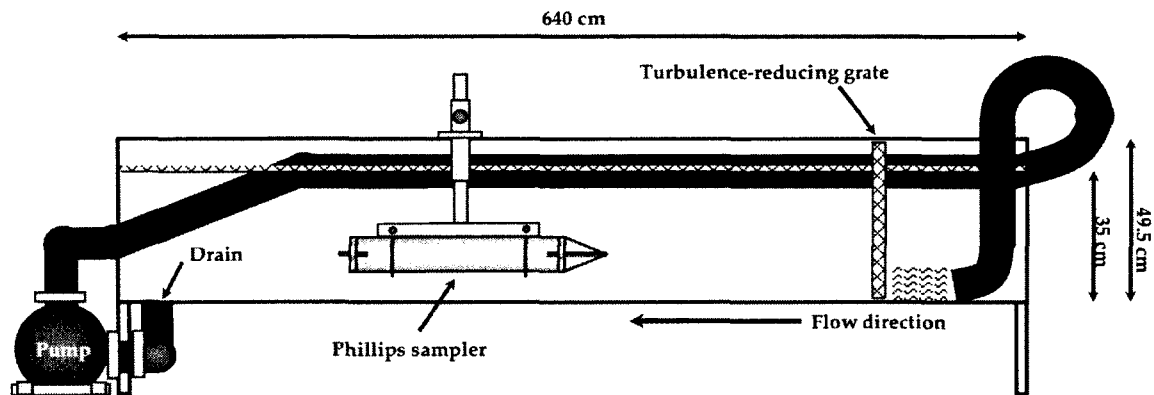


Fig. 2.3 Flume-based calibration of the Phillips suspended sediment sampler. The pump recirculates water and sediment in the flume to maintain continuous flow. The turbulence-reducing grate is used to buffer the turbulent water entering the flume from the recirculation tube (figure not to scale).

A Swoffer 2100 current meter was used to determine that the average velocity in front of the Phillips sampler inlet tube was 0.28 m s^{-1} . This value is similar to the flow velocity used in the Phillips *et al.* (2000) evaluation (0.3 m s^{-1}), which was deemed representative of river flow during storm events at the UK field sites used in that study. Leopold (1997) suggests a flow velocity of about 0.4 m s^{-1} is representative of many small streams and creeks, and flow proportionately increases through larger creeks and tributaries, until the low flow range is $\sim 1 \text{ m s}^{-1}$ to 1.5 m s^{-1} in the main channel. Therefore, given the logistical problems often encountered in generating high velocities in artificial flumes, a mean flow velocity of 0.28 m s^{-1} may be considered as representative of the small creeks sampled in the QRB, but may not be entirely representative of the main Quesnel River, especially during peak flows.

2.2.3 Experimental procedures

Two sediment types were used in the calibration tests: (i) scientific-grade kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5$), i.e. clay-sized material; and (ii) Quesnel River sediment collected near site Q1 and wet sieved to $180\ \mu\text{m}$. Kaolinite was chosen primarily to assess the sampler's efficiency in collecting sediment mass (i.e. collected mass compared to expected mass retained), while Quesnel River sediment was used to assess the size preferentiality of the sampler (i.e. is the collected sample representative of all particle sizes in suspension or does the sampler select for coarser or finer sediment?). The results of the trials involving (ii) may have implications influencing the interpretation of data obtained from the sampler; e.g. is all sediment entering the sampler retained or do some finer particles remain in suspension and exit the trap? Is this expressed by a coarser sampler d_{50} grain size in comparison to ambient d_{50} ?

Both the kaolinite and river sediment samples were diluted to 5 mg in 500 mL of distilled water and sonified using a Branson 1510 ultrasonic bath for five minutes to break up any composite particles or flocs and promote homogeneous hydrodynamics of the sediment (Rex & Petticrew, 2008). Prior to the commencement of each trial, 200 g of sediment was introduced to the flume and allowed to fully disperse. As with the field methods (section 3.3.1), the Phillips sampler was then filled with flume water (river water in field), capped at each end, and secured at 0.6 of depth, pointing into the flow. Using 200 g of sediment in the volume of water in the flume set-up created an ambient suspended sediment concentration (SSC) in the flume of $161\ \text{mg L}^{-1}$, which is representative of other temperate rivers during moderate to high flow conditions (Wass & Leeks, 1999).

Each experimental trial lasted six hours and three trials were conducted for each sediment type. One litre grab samples were taken adjacent to the trap at 0 hours (h), 2h, 4h, and 6h to be analyzed for SSC. This procedure enabled any settling of sediment during the trials to be identified and accounted for in the calibration. At the end of each trial the contents of the Phillips sampler were rinsed out using distilled water and collected in a 10 L plastic bucket.

2.2.4 Analytical procedures

Material collected by the Phillips sampler was allowed to settle (usually over 24 h) in the buckets and the supernatant was removed by siphoning. Wet samples were then transferred to pre-weighed whirl-paks and freeze-dried at UNBC. After sediment dry mass was measured, sub-samples were removed for particle size analysis. Sub-samples underwent digestion with hydrogen peroxide prior to analysis to remove organics and induce dispersion. Particle size characteristics for both flume experiment and field-derived (see Chapter 3 for field deployment and analysis preparation procedures) sediments were determined using a Malvern Multisizer Hydro 2000G at Simon Fraser University, BC.

Grab samples collected during each trial were passed through a glass microfiber filter (0.7 μm mesh) to separate the sediment from water. Samples were then dried and weighed enabling an estimation of SSC.

2.2.5 Expected sediment retention

To evaluate the sediment mass efficiency of the Phillips sampler the expected sediment retention for each sediment type (i.e. kaolinite and Quesnel River) was calculated (see Appendix A1 for further details). In lab-based experiments, the Phillips sampler was found to be non-isokinetic (Phillips *et al.*, 2000). Thus, in order to determine the comparatively slower flow velocity within the sampler, as dictated by friction and inertial forces in the inlet tube, the following equation, developed in Phillips *et al.* (2000) through laboratory-based experimentation, was used (Eq. (2.1)):

$$y = -2.182 + 2.074(x) \quad (2.1)$$

where y is the logarithmic flow velocity in the Phillips sampler inlet tube, and x is the logarithmic flow velocity of the flume.

By determining the product of the inlet tube flow velocity, the inlet tube cross-sectional area, the trial duration, and the internal volume of the Phillips sampler (to account for initial SSC), the volume of water passing through the sampler during each trial was calculated. The rate at which the volume of water in the Phillips sampler was replaced during each 6 h trial was found by dividing the sampler internal volume by the sampler discharge (i.e. product of the inlet tube flow velocity and the inlet tube cross-sectional area).

With the above information, two methods of calculating expected sediment retention were explored. The versions were abbreviated to (1) temporal-based and (2) grab sample-based. In the temporal-based method, sediment retention in the Phillips sampler is a function of the volume of water that flows through the sampler and the assumption that all sediment is retained in the sampler during each “flush”. As the

SSC in the flume water decreases during each trial (because of sediment retention in the sampler) it is necessary to account for this reduction, and this was described by Eq. (2.2):

$$\sum^n [\text{SSC} \cdot V_s] \quad (2.2)$$

where SSC is suspended sediment concentration (mg L^{-1}), V_s is sampler volume (L) and n is the number of times the water in the sampler is replenished. This calculation determined the mass of sediment removed from SSC for each sampler “flush”, enabling a more accurate calculation of sampler sediment retention efficiency.

The grab sample-based method was a modified version of the temporal-based method (just described) but instead incorporated the SSC values determined from grab samples taken adjacent to the sampler at 2h intervals. This approach allowed for the observed changes in SSC due to settling (described further below). The initial SSC (time = 0h) was higher in most trials than the proceeding three values, which displayed little variation and appeared stable. Therefore, an average of the 2h, 4h, and 6h values for each trial was determined and termed the *stabilized SSC* and used in calculations for SSC passing through the Phillips sampler after the initial decrease in SSC. The expected sediment retention was then calculated by adding the products of the initial SSC and the volume of the sampler (iteration 1, i.e. first flush of water passing through the sampler) and the stabilized SSC, the volume of the sampler, and the remaining iterations (i.e. subsequent flushes of water through the sampler during the remainder of the trial).

2.3 Results and discussion

Results of the sediment grain size distribution and mass retained by the Phillips sampler are compared to ambient values to assess sampler efficiency below. Similarities to results of the Phillips *et al.* (2000) evaluation are also discussed. Deviations from anticipated ambient values for sediment mass efficiency, using both temporal and grab sample-based methods, are evaluated. As another check of the efficiency of the Phillips sampler, the particle size composition of sediment collected by the sampler deployed in the field in the QRB is also compared to equivalent data for adjacent channel bed sediment samples (sieved to $<62.5\ \mu\text{m}$, see Chapter 3).

2.3.1 Grain size efficiency

2.3.1.1 Flume evaluation of grain size efficiency

In the controlled appraisal of the Phillips sampler at the QRRC flume, median grain sizes (d_{50}) of kaolinite and river sediments were measured at $6.8\ \mu\text{m}$ and $99.5\ \mu\text{m}$, respectively, prior to introduction into the flume. Assuming complete homogenization of grain sizes and continuous suspension of sediment in the flumes, these values were expected to be representative of flume d_{50} during the Phillips sampler evaluations. Although this was likely valid for the kaolinite trials, sedimentation was observed during river sediment trials, suggesting that the actual flume suspended load for the latter was finer than the above measurement. Specifically, in the river sediment trials, settled material was visually observed on the flume bottom with some concentration toward the less turbulent water near the drain and away from the recirculation outflow.

The d_{50} distribution results for sampler-retained and flume sediments are presented in Figures 2.4 and 2.5. The kaolinite samples retained by the Phillips sampler

(i.e. mean $d_{50} = 15.9 \mu\text{m} \pm 0.5$ standard error) were coarser compared to ambient values (i.e. $6.8 \mu\text{m} \pm 0.2$), while the d_{50} of river sediment collected was finer (i.e. $47.2 \mu\text{m} \pm 1.8$) than the measured flume suspended sediment (i.e. $99.5 \mu\text{m} \pm 0.2$). Sediment (both kaolinite and river) was initially sieved to $<180 \mu\text{m}$ as opposed to $<62.5 \mu\text{m}$ in an attempt to determine whether grain sizes above the sand-silt boundary, but still potentially capable of sustained suspension, would be captured by the Phillips sampler. In the case of the river sediment trials, the flume flow velocity was probably insufficient for continued suspension or re-entrainment, and a visible portion of the sediment settled out during each trial. This is a possible explanation for the finer material collected by the sampler compared to the mean d_{50} measured in the flume.

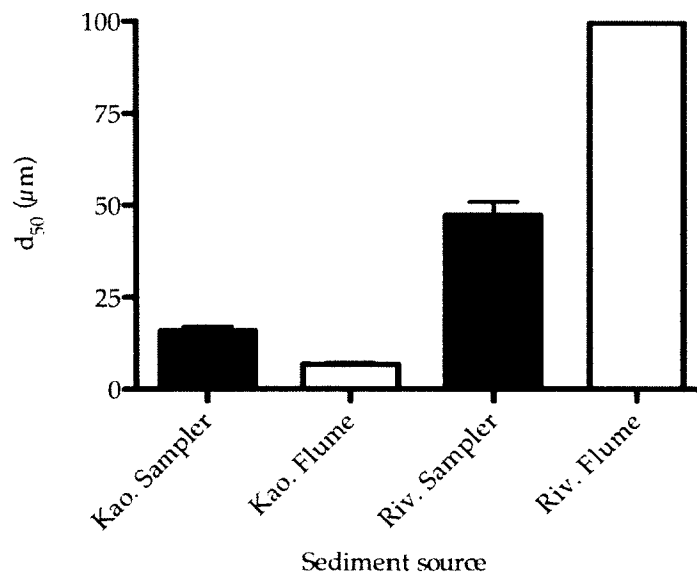


Fig. 2.4 Comparison of grain size (d_{50}) between sediment retained by the Phillips sampler and that suspended in the flume for both kaolinite (Kao.) and Quesnel River (Riv.) sediment types. Note that the Phillips sampler appears to oversample coarser sediment during the kaolinite trials and finer sediment during the river trials.

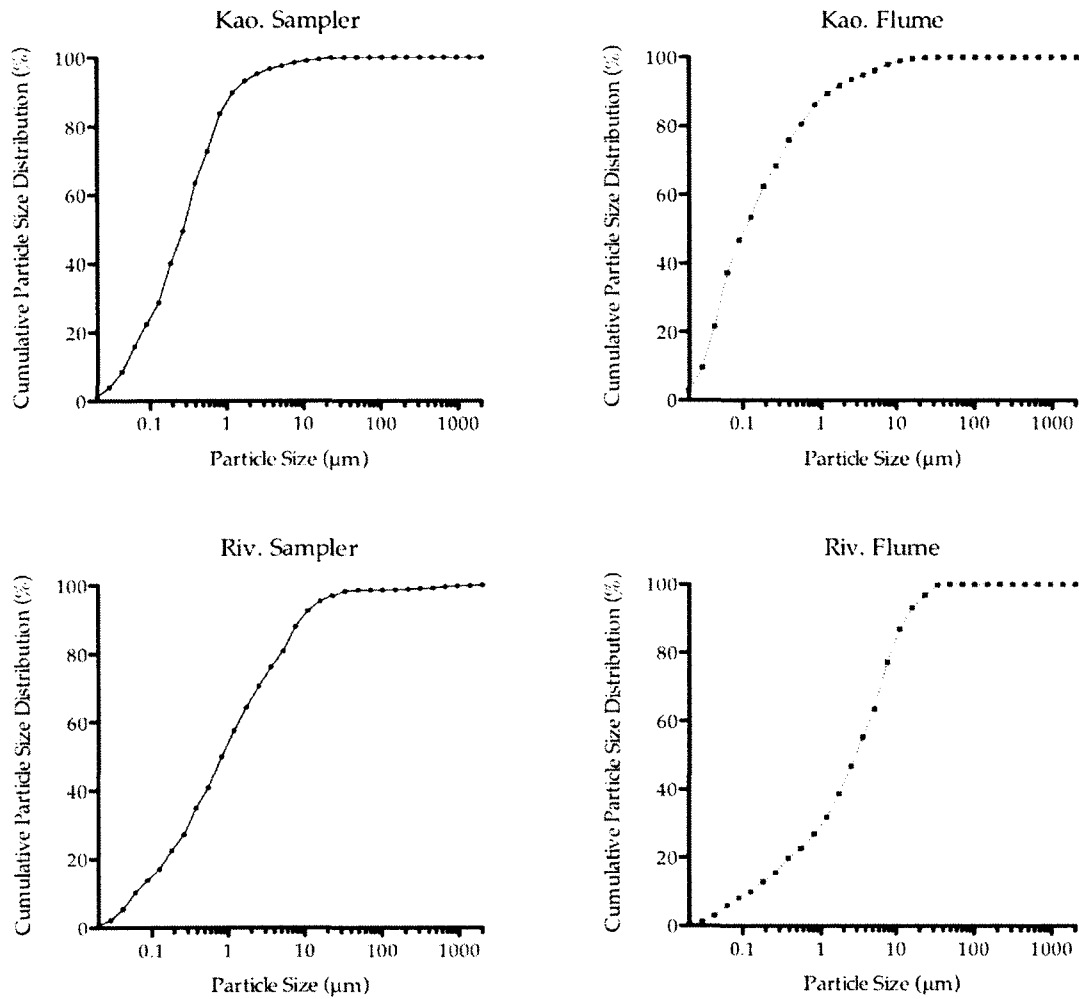


Fig. 2.5 Particle size spectra for sediment retained by the Phillips sampler and flume suspended sediment for both kaolinite (Kao.) and Quesnel River (Riv.) sediment types.

For the kaolinite trials, it is apparent that some coarsening of sampler-retained sediment in relation to flume suspended load occurred. Similar results were recorded in Phillips *et al.* (2000), with flume flow velocity at 0.3 m s^{-1} . Preferential selection of coarser sediment by the sampler compared to flume sediment was observed and could be due to: (1) through-flow or sustained suspension within the Phillips sampler of finer particles; and (2) greater retention of suspended sediment with a coarser d_{50} as found in Phillips *et al.* (2000). A third reason is that some floccu-

lation and aggregation occurred after both types of sediment (especially the kaolinite) were introduced to the flume. This could result in the measurement of coarser sediment particles (i.e. composite particles), and hydrodynamic alterations to the sediment particles (i.e. changes in size and density), which would influence settling rates and sampler retention.

Thus, sediment coarsening between flume and sampler-retained samples with kaolinite can be explained by through-flow and preferential selection by the sampler for coarser particles, and perhaps by flocculation. The sediment fining observed between flume and sampler-collected samples for river sediment is likely due to settling of the coarsest portion of the flume sample due to problems with the flume set-up and a significantly finer continuous suspended load for most of the trials.

2.3.1.2 Comparison between sediment collected by the Phillips sampler and adjacent channel bed sediment

In order to assess the ability of the Phillips sampler to collect a grain size distribution representative of the ambient suspended sediment load in the natural environment, it was necessary to compare the d_{50} values for the sediment retained by Phillips samplers deployed in the field with those from equivalent samples collected directly from the channel using an independent approach (i.e. time-integrated samples collected another way). However, such independent time-integrated suspended sediment samples were not collected during the 2008 field season. As a surrogate, bed sediment samples taken adjacent to individual Phillips samplers, and sieved to $<62.5 \mu\text{m}$, were used. Since Phillips sampler-retained sediment was also sieved to $<62.5 \mu\text{m}$ (for subsequent geochemical analysis; Chapter 3), an assessment of grain size efficiency is possible. The use of bed sediment samples as suitable surrogates for sus-

pendent sediment samples has been used in numerous studies (e.g. Horowitz & Stephens, 2008), as the surface sediment deposited on the channel bed is mainly composed of settled (former) suspended sediment.

Values of the d_{50} associated with the sediment collected by the Phillips sampler and values for spatially comparable bed sediment are presented in Table 2.1. Comparisons are organized by land use-association (i.e. in-line with the approach adopted in this research project).

Table 2.1 Comparison of d_{50} for sediment collected by the Phillips sampler and for channel bed sediment samples. Samples are organized by land use (forestry (F), agriculture (A), mining (M), control (C) and Quesnel River (Q)). Standard error (in parentheses) and the difference between sediment types (Phillips sampler – Bed) are also presented.

Sediment source	Phillips sampler d_{50} (μm)	(n)	Bed d_{50} (μm)	(n)	Difference (μm)
F	15.9 (± 1.6)	15	12.1 (± 0.0)	3	3.8
A	14.9 (± 3.0)	18	13.4 (± 2.2)	12	1.5
M	20.0 (± 5.6)	12	15.6 (± 6.3)	6	4.4
C	19.0 (± 3.0)	21	21.8 (± 3.3)	12	-1.8
Q	9.9 (± 1.7)	15	16.2 (± 2.3)	21	-6.3

Here, Phillips sampler-retained sediment d_{50} values are subtracted from equivalent channel bed sediment d_{50} values to highlight any preferential selection for finer or coarser sediment by the samplers. While it is important to recognize that the bed sediment (although sieved to $<62.3 \mu\text{m}$) is not exactly the same as the suspended sediment during the time in which the Phillips samplers were deployed in the field (i.e. it is a surrogate), in general, there was little difference between sediment captured by the Phillips sampler and channel bed sediment. The greatest coarsening was found in the mining channels ($4.4 \mu\text{m}$), and the most pronounced fining was exhibited in the samples from the Quesnel River main channel ($-6.3 \mu\text{m}$).

The Mann-Whitney U -test was applied to the data and revealed no significant differences between samples for all land uses tested. It was not possible to test F and

M due to the small sample sizes (i.e. less than the $n=3$ minimum required for the test). As with the Phillips *et al.* (2000) study, field-based grain size comparison between sampler-retained and ambient suspended sediment are statistically similar, prompting the conclusion that the Phillips sampler, in this instance, is capable of collecting a representative sample of the ambient suspended sediment load, especially for smaller creeks and streams.

2.3.2 Mass efficiency of the Phillips sampler

Two methods were used to determine the mass efficiency of the Phillips sampler. The first, identified as the *temporal method*, involved a calculation of sediment retained by the Phillips sampler assuming an initial ambient SSC of 0.161 g L^{-1} and accounting for ambient SSC decreases over time due to sampler retention. In the second approach, deemed the *grab sample method*, the initial ambient SSC and a lower, “stabilized” SSC level were based on grab sample-derived values; thereby accounting for observed settling in the flume set-up. It should be noted that non-homogenous turbulent flow was observed within the flume despite an attempt to mitigate this using a turbulence and eddy-homogenizing grate. This has also been identified in Phillips *et al.* (2000) as a potential source of error and cause of decreases in sediment retention by the sampler.

Table 2.2 presents the grab sample SSC values over time and the 0 h – 6 h and 2 h – 6 h means for each trial (i.e. kaolinite 1-3 and river 1-3). The latter mean values represent the stabilized SSC for each trial.

Table 2.2 Incremental grab sample SSC values during the flume trials. Most sediment materials, excluding Kao 2 and Kao 3, exhibit a higher 0h SSC relative to 2h-6h, which display low inter-grab sample variability. Mean SSC values for 0h-6h and 2h-6h were calculated to highlight this drop-off and the stabilization of SSC values over time. Standard error values are presented in parentheses.

Sediment type	Grab sample SSC (mg L^{-1}) at time:				Mean (mg L^{-1}) 0 h - 6 h	Mean (mg L^{-1}) 2 h - 6 h
	0 h	2 h	4 h	6 h		
Kao. 1	141.1	137.2	131.4	132	135.4 (± 2.3)	133.5 (± 1.8)
Kao. 2	132.8	139.1	132.7	138.6	135.8 (± 1.8)	136.8 (± 2.1)
Kao. 3	137	139.6	134.8	134.6	136.5 (± 1.2)	136.3 (± 1.6)
Riv. 1	66.5	27.3	24.2	24.4	35.6 (± 10.3)	25.3 (± 1.0)
Riv. 2	84.2	19.3	18.3	15.7	34.4 (± 16.6)	17.8 (± 1.1)
Riv. 3	72.6	15.8	18.9	19.5	31.7 (± 13.7)	18.1 (± 1.2)

There is relative consistency among grab sample SSC for the kaolinite trials, while Quesnel River sediment trials exhibited a distinct drop in SSC after the initial ($t = 0\text{h}$) collection. In general, greater settling occurred with the Quesnel River sediment. This is illustrated in both the grab samples and total sediment values (presented earlier). Consequently, sediment retention (i.e. mass and particle size) during the kaolinite trials is expected to be more efficient than during the river sediment trials. The comparative results of the temporal and grab sample methods are presented in Figure 2.6.

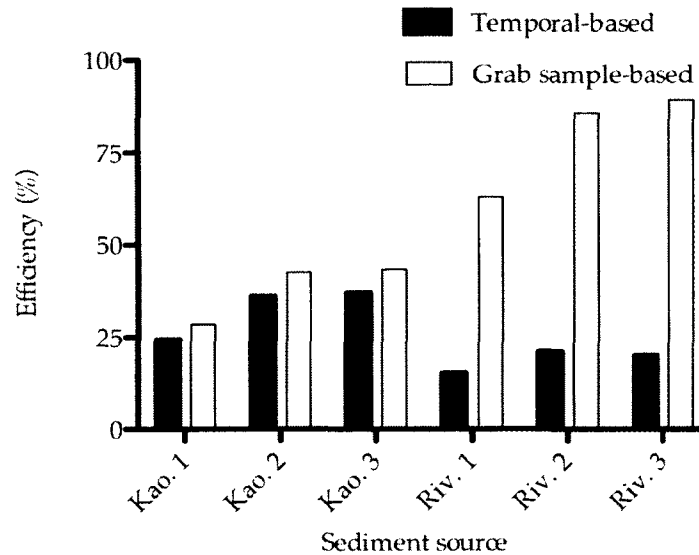


Fig. 2.6 Efficiency of the Phillips sampler to collect sediment mass using temporal-based and grab sample-based calculation methods. Note that sample efficiency increases marginally for kaolinite (Kao.) trials (+4.2% - 6.5%) compared to river sediment (Riv.) trials (+47.7% - 69.1%) between temporal and grab sample calculation methods.

The temporal method, as a means to determine sediment retention efficiency of the Phillips sampler, is appropriate in an experiment with complete suspension and homogenization of sediment. Using this method, in this study, the kaolinite trials proved more efficient than river trials in retaining sediment 3.2% to 21.7%. The maximum efficiencies of sediment mass collected by the Phillips sampler (i.e. collected vs. expected retention) were 37% for kaolinite and 15.3% for river sediment.

Using the grab sample method, the sampler efficiencies were higher and arguably more valid than with the temporal method. What is not evident is why the QRB evaluation for each sediment type showed lower sampler efficiencies for the first trial and similar, higher efficiencies for the 2nd and 3rd trials. The conditions were the same in all cases and the flumes were flushed of all sediment between trials. The mean efficiencies (trials 2 and 3 only) for kaolinite and river sediment were 43% and 87.4%, respectively.

When the grab sample method results are compared to the Phillips *et al.* (2000) sampler sediment mass efficiency results (i.e. 46% for finer sediment and 71% for coarser sediment, at 0.3 m s^{-1}), the mean QRB values are 7.9% less efficient for kaolinite and 8.2% more efficient for river sediment, respectively. Thus, coarser flume suspended load was captured by the Phillips sampler more efficiently during the sampler evaluation, and provided a more representative sample.

2.4 Conclusions

The Phillips time-integrated suspended sediment sampler was evaluated for sediment mass and grain size efficiency in a series of flume-based trials with two varieties of sediment. Grain size efficiency was also tested using field-derived (i.e. sampler vs. channel bed sediment) data. Preferential selection by the Phillips sampler for coarser sediment was recorded in the kaolinite trials but not for the field-based evaluations, which were closely representative of flume conditions. Settling of some of the introduced suspended load occurred in the flume-based trials for the Quesnel River sediment. This was confirmed by grab sample-derived SSC values, which showed a large initial decrease in SSC due to the settling of the coarser river sediment at the start of the trials, and was accounted for in the grab sample-based method during mass efficiency analysis.

For both sediment types, the efficiencies of the Phillips sampler were similarly to the initial Phillips *et al.* (2000) evaluations. Inefficiencies in sample collection were accounted for by through-flow in the sampler of very fine-grained sediment, and, in the case of river sediment trials, settling of the coarsest grains on the flume bottom.

It was demonstrated that the Phillips sampler is able to collect a time-integrated sample of suspended sediment that is broadly representative of flume conditions, particularly in terms of its particle size distribution. There are, however, some important caveats to consider that influence interpretation of the nature of the sediment collected. The flume and field (i.e. bed sediment) evaluations validate the choice of the Phillips sampler as the main field equipment for this study. However, to improve upon the existing model a variable anchorage apparatus, as presented in McDonald *et al.* (2010), should be considered.

CHAPTER 3: SEDIMENT-ASSOCIATED CONTAMINANT CONCENTRATIONS

"In many countries, water-quality regulatory limits are based solely on the dissolved (water processed through a 0.45 μm filter) phase of a wide variety of chemical constituents, even though their sediment associated counterparts can be orders of magnitude higher." (Horowitz, 2008)

3.1 Introduction

This chapter describes the collection and analysis of suspended and bed sediment samples from the QRB in Northern BC. Samples representing predominant land use types (e.g. forestry, agriculture, mining) and control inputs were collected and analyzed for a suite of potential contaminants. These contaminant concentration values were subsequently compared to background geology to confirm the anthropogenic origin of elevated values and to sediment quality guidelines (SQGs) to quantify potential metal and nutrient toxicity based on accepted standards. This addresses objective one of the study: to determine the contaminant concentrations of fine suspended sediments (and some limited channel bed samples) associated with different land use activities (see section 1.2.) The goal is to quantify the health of the QRB in terms of fine sediment ($<62.5 \mu\text{m}$) quality, and to identify specific anthropogenic influences threatening aquatic health in the basin.

3.2 Methods

3.2.1 Field sampling

In the field, both suspended and bed sediment samples were collected. As the prime focus of this chapter is to quantify fine suspended sediment-associated contamination, an emphasis was placed on suspended sediment collection using the Phillips sampler (Phillips *et al.*, 2000). Bed sediment was used as a basis for assessing

the efficiency of the Phillips sampler (Chapter 2), and to determine geochemical partitioning between bed and suspended sediments (Chapter 4) within the fluvial environment; that is, whether or not the same geochemical elements, in the same concentrations, were attaching to both suspended and stored channel bed sediments.

3.2.1.1 Suspended sediment collection

Suspended sediment samples were collected using time-integrated samplers in stream reaches draining the following land use activities: forestry, agriculture, and mining. Samplers were deployed at sites where the area upstream was dominated (>50%) by a particular land use (e.g. forestry or agriculture) or by a point-source activity likely to influence the sediment in the stream (e.g. mining). Control sites represented natural forest with a minimum of anthropogenic disturbance. However, at least one road is known to cross each control sub-basin and much of the region has been previously deforested, therefore it is not possible to claim with full certainty that control (or reference) sites represent pristine forests.

Two sampling sites were located on the main stem of the Quesnel River. Site Q1 was located at the UNBC Quesnel River Research Centre (QRRRC) and represents the outflow of Quesnel Lake. Site Q2 was located near the town of Quesnel at the river mouth, and is considered representative of contributions from the entire upstream basin, particularly those downstream of the lake.

Sediment samples were collected from each of the 13 sites at monthly intervals over the snow-free period of May 2008 to October 2008. Collecting sediment over a month enabled a sufficient amount of sediment to be retained by each Phillips sampler to allow laboratory analysis (~1 g minimum), while also enabling an assessment of temporal changes in concentrations in the different sub-basins.

The initial deployment and final removal of traps over the six-month field season was dictated by spring thaw (i.e. freshet) and late-fall drought and/or freeze timing. Seven of 13 sites were accessed by raft exclusively, while the remaining six sites were road and foot accessible. However, the initial sampling interval, beginning in April, required snowmobile access, as the early spring snowpack made the roads impassible by other means.

At the end of each sample period the contents of each sampler were washed out on-site using distilled water, and collected in a sealable 10 L plastic bucket. The buckets were pre-disinfected using phosphorus-free cleaning agents (i.e. to avoid contamination of samples by P with most normal detergents). Samplers were then returned to their rebar moorings and depth was adjusted for monthly stage changes.

Despite precautions taken during the site planning process some samples were lost, leaving gaps in the data set. Specifically, two Phillips samplers were lost due to insufficient mooring during freshet (i.e. sites Q2 and A1), and some channels, although promising during April reconnaissance, proved ephemeral and dried-up during fall sampling periods (i.e. sites F1, F3, and M3). However, samples from all land use types were still collected during all sample periods, and completion of project goals was not hindered.

After collection, samples were allowed to settle for 24 h at the QRRC prior to the removal of the supernatant by siphoning. To facilitate analysis of the fine-grained fraction, samples were wet sieved to $<62.5\ \mu\text{m}$ (Walling & Woodward, 1992), secured in Nasco Whirl-paks, and frozen. In order to best preserve chemical integrity all samples were processed and frozen within 72 h of collection. Finally, sediment samples collected from sites in the QRB were freeze-dried at UNBC for preservation.

3.2.1.2 Channel bed sediment collection

It is well recognized that a fraction of fine sediment is deposited and retained in the channel bed (Horowitz & Stephens, 2008). In order to geochemically characterize fine sediment in both suspended and storage phases, select samples of channel bed sediment were collected adjacent to each Phillips sampler during the second half of the 2008 field campaign (July-August, September-October). Due to this late season sampling, fewer bed sediment than suspended sediment samples were collected. In all, 21 land use-associated (i.e. F, A, M, C) channel bed samples were collected. It was not possible to collect bed sediment at sites F1 and F3, leaving site F2 as the only representative of the forestry input with two samples. Replicate analysis was possible for all other land use types with two samples for each of sites A1, A2, M1, M2 and M3 and three samples for each of sites A3, C1 and C2.

Using a re-suspension method (Lambert & Walling, 1988; Walsh *et al.*, 2007) bed samples were collected for each land use-associated sub-basin. Samples were preserved for future analytical analysis using the procedures outlined above (i.e. section 3.2.1.1).

3.2.2 Laboratory analysis

In the Central Equipment Laboratory at UNBC, a range of base cations, heavy and trace metals, and nutrients, totaling 32 geochemical properties, were selected for analysis. Geochemical properties were chosen to represent a range of identified aquatic contaminants (Luoma & Rainbow, 2008). Samples underwent acid and microwave digestion using nitric and hydrochloric acids. Concentrations (in μg of a given geochemical element per g of dry sediment) were then determined using in-

ductively coupled plasma mass spectrometry (ICP-MS). In this chapter, the focus is on results for arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), phosphorus (P), selenium (Se) and zinc (Zn), in correspondence with those elements with available sediment quality guideline (SQG) values.

3.3 Results and discussion

QRB land use-associated contaminant concentrations are compared to background geology values using the BC drainage geochemical atlas (Lett *et al.*, 2008). Similar comparisons are made to geochemical values for the Earth's continental crust and to Great Lakes pre-colonial sediment. To quantify river health, QRB suspended and bed sediment-associated values are compared to international, national, and provincial SQGs. Based on these comparisons, the sources and environmental threat level of contaminant concentrations in the QRB are presented and discussed.

3.3.1 Background geology

It is important to compare the concentrations of sediment-associated metals and nutrients measured in this study to those available from regional geochemical databases so as to determine if, and to what degree, concentrations are elevated relative to what might be found naturally. Collected metal and nutrient concentrations were therefore compared to their counterparts in the underlying geology of the QRB, using the BC drainage geochemical atlas (Lett *et al.*, 2008) (Tables 3.1 & 3.2).

Table 3.1 QRB sample site coordinates and associated rock types determined using the BC drainage geochemical atlas. Actual atlas bedrock sample collection locations are not identical to QRB sample sites, but are spatially representative alternatives. The distance between actual and QRB sample locations is also presented.

Site	Latitude	Longitude	Deviation from <i>Lett et al.</i> (2008) sample (m)	Rock Type
F1	52.751778°	-122.125919°	1860.71	Undivided sedimentary rocks
F2	52.806800°	-122.173247°	129.94	Intrusive rocks, undivided
F3	52.811472°	-122.167364°	607.71	Intrusive rocks, undivided
A1	52.788847°	-122.170369°	379.16	Undivided sedimentary rocks
A2	52.823558°	-122.192942°	1368.04	Undivided sedimentary rocks
A3	52.857383°	-122.253297°	2273.03	Intrusive rocks, undivided
M1	52.495268°	-121.513290°	226.94	Calc-alkaline volcanic rocks
M2	52.631164°	-121.643083°	542.93	Basaltic volcanic rocks
M3	52.660900°	-121.791522°	1649.87	Volcaniclastic rocks
C1	52.555417°	-121.550895°	305.72	Basaltic volcanic rocks
C2	52.756736°	-122.153081°	273.95	Undivided sedimentary rocks
Q1	52.619378°	-121.587719°	1562.05	Basaltic volcanic rocks
Q2	52.996028°	-122.442044°	5178.12	High level quartz phyric, felsitic intrusive rocks

Table 3.1 presents the predominant rock type for each land use-specific sub-basin. The actual QRB sample site locations were not used in the data collection for the BC drainage geochemical atlas, so the best surrogate locations in the atlas' database (see <http://www.empr.gov.bc.ca/>) were used (maximum distance = 5.2 km, mean distance = 1.3 km). Therefore, the rock types and elemental concentrations presented in Tables 3.1 & 3.2 should be interpreted with some caution, as the possibility of local variations cannot be eliminated.

Table 3.2 BC drainage geochemical atlas elemental concentrations ($\mu\text{g g}^{-1}$ dry weight) for each land use-associated QRB sampling site (based on data in Lett *et al.*, 2008).

Site	Element										
	As	Au	Co	Cu	Fe	Mn	Mo	Ni	Pb	U	Zn
F1	6.0	4	10	30	1.70	390	1	30	1	1.5	64
F2	4.5	3	8	23	1.55	365	1	21	2	2.0	40
F3	4.5	3	8	23	1.55	365	1	21	2	2.0	40
A1	6.0	10	8	22	1.80	370	1	26	1	2.0	58
A2	16.5	8	10	36	1.70	310	1	38	1	2.0	122
A3	3.0	15	10	21	1.55	475	1	30	1	2.5	48
M1	4.5	8	7	24	1.60	420	1	9	1	1.5	38
M2	4.5	4	12	56	2.50	710	1	26	4	1.5	44
M3	17.5	2	8	44	1.80	690	1	10	2	3.0	46
C1	1.5	3	11	52	1.85	310	1	22	4	1.0	38
C2	7.0	2	10	31	1.90	520	1	20	1	1.0	62
Q1	6.0	2	19	78	3.40	1600	1	122	4	1.0	54
Q2	3.0	44	7	19	1.40	280	1	19	1	4.0	34

The background geochemical concentrations for each site are presented in Table 3.2 ($\mu\text{g g}^{-1}$ dry weight). Of interest are the comparatively high values for Co, Cu, Fe, Mn and Ni associated with site Q1. Site M2 also stands out with elevated levels of Fe and Mn, and site A2 displays an elevated value for As and the highest individual concentration for Zn. Also of note are As and Mn for M3, and Au and U for Q2. All of which suggest elevated site-specific baseline concentrations relative to mean baseline values (see Table 3.3, far right column). Nonetheless, the values presented in Table 3.2 provide a useful way to assess the impact of underlying bedrock and surficial material on the geochemical content of the sediment samples collected from the study sites (i.e. Table 3.3).

Table 3.3 Comparison between mean suspended sediment-associated element concentrations for the QRB study sites and regional, national and global background values determined from other studies. All values are presented in $\mu\text{g g}^{-1}$ dry weight. Note that geochemical atlas of BC values represent averages from all study sites (see Table 3.2).

Elements	Land use				Earth's continental crust ^a	Great Lakes pre-colonial sediment ^b	BC drainage geochemical atlas (mean values) ^c
	F	A	M	C			
Metals							
As	9 ± 0.74	11 ± 0.57	15 ± 2.08	9 ± 1.52	1.7	4	6.5 (± 1.4)
Cd	0.8 ± 0.26	0.7 ± 0.06	0.6 ± 0.09	0.5 ± 0.09	0.1	1	–
Cr	67 ± 3.95	61 ± 2.19	48 ± 3.13	63 ± 4.30	126	31	–
Cu	147 ± 49.2	78 ± 9.23	116 ± 10.5	92 ± 17.4	25	25	35.3 (± 4.9)
Hg	0.22 ± 0.09	0.1 ± 0.02	0.16 ± 0.03	0.08 ± 0.01	0.04	0.1	–
Mn	740 ± 48.4	3584 ± 1737	1570 ± 195	1886 ± 424	716	400	523.5 (± 97.3)
Ni	41 ± 2.64	43 ± 1.75	39 ± 7.45	39 ± 2.53	0.0004	31	30.3 (± 8.0)
Pb	22 ± 6.75	14 ± 1.46	10 ± 0.66	10 ± 0.89	14.8	23	1.9 (± 0.4)
Se	2.0 ± 0.32	1.7 ± 0.07	3.1 ± 0.35	1.5 ± 0.07	0.12	–	–
Zn	262 ± 87.8	180 ± 54.4	144 ± 24.9	117 ± 14.7	65	65	52.9 (± 6.3)
Nutrients							
P	1077 ± 114	896 ± 18.5	1217 ± 89.3	950 ± 64.7	757	–	–
n	14	16	15	11			

^a Wedepohl (1995)

^b Fletcher et al. (2008)

^c Lett et al. (2008)

Table 3.3 compares the mean element concentrations for the QRB study sites (describe in section 3.2.1.1) with the mean values for the Earth's continental crust, the Great Lakes pre-colonial sediment, and the BC drainage geochemical atlas. The number of elements presented (compared to those actually analysed) was determined by those elements available in the datasets. Although only comparable to con-

tinental crust, values were added for two elements thought to be of regional interest: P (often associated with agriculture) and Se (often associated with mining activities).

In general, QRB mean land use values exceed all three geological baseline values in Table 3.3. However, there were a few exceptions. The continental crust value for Cr of $126 \mu\text{g g}^{-1}$ exceeded all four land use concentrations, suggesting a higher global concentration than was expected for Canadian or BC basins, and/or limited breakdown (e.g. weathering) and transfer from continental crust to overlying soils and sediment. For Pb, most land use-associated concentrations fell below the continental crust baseline (forestry being the only exception) and all were less than the Great Lakes sediment-associated value of $23 \mu\text{g g}^{-1}$. This appears to be due to a lower local baseline for Pb of $1.9 \mu\text{g g}^{-1}$ for the QRB, which is consistent with all land use-associated values (Table 3.2). Also of note, is that all land use means for Cd were less than the Great Lakes sediment value but exceeded that of the continental crust.

3.3.2 International, national, and provincial sediment quality guidelines

It is standard practice to compare sediment-associated contaminant concentration data to recognized SQGs. These guidelines are used in many practical applications, including the interpretation of historical geochemical data, sediment quality assessments, ecological risk and remediation assessments, and in planning sediment quality remediation initiatives (Long & Morgan, 1991). Remembering that the goal of this chapter is to determine the contaminant concentrations of fine suspended sediments associated with different land use activities in the QRB, guidelines provide a means of quantifying the level of contamination.

Wennings & Ingersoll (2002) suggests that most SQGs are derived from two

predominantly laboratory-based methods: (1) mechanistically based SQGs use laboratory *spiked* (with contaminants) sediments and (2) empirically based SQGs compare large databases of similar sediment toxicity and chemistry tests. Both methods then compare results with field-collected samples. Typically element toxicity is evaluated based on the sensitivity of different benthic organisms to chemical contaminants. The mayfly (*Hexagenia*) is commonly used in these evaluations as an organism comparably sensitive to contaminated aquatic environments (Fletcher *et al.*, 2008). Field sampling usually involves bulk bed sediment collection without sieving or further allowance for contaminant concentration-influencing factors such as organic matter content or particle size (MacDonald *et al.*, 2000). Therefore, raw or uncorrected data for the suspended and bed sediment samples collected in this study provided the most appropriate basis for comparison to SQGs.

Of the 34 heavy and trace metal and nutrient concentrations analyzed through ICP-MS, only 11 were found in numerous SQGs. Therefore, a condensed field of elements with consensus-based levels of toxicity was available. This is due to a focus of research during SQG creation on a limited number of indicator or key metals (Long & Morgan, 1991; Persaud *et al.*, 1993; Smith *et al.*, 1996; CCME, 2002; Luoma & Rainbow, 2008), while including several polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and organochlorine pesticides. These decisions were made to select for sediment-associated chemicals of greatest potential concern in freshwater environments. In light of these restrictions, values for the metals As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, and Zn, and the nutrient (total) P, for both suspended and bed sediment, were compared to a variety of SQGs (Tables 3.4 & 3.5).

Table 3.4 Comparison of mean suspended sediment metal and P concentrations ($\mu\text{g g}^{-1}$ dry weight) for different land use activities to sediment quality guidelines: TEC, threshold effect concentration; PEC, probable effect concentration; ISQG, interim sediment quality guidelines; PEL, probable effect level; LEL, lowest effect level; SEL, severe effect level; FAC, freshwater ambient criteria. Values in bold represent potentially toxic concentrations and are discussed in the text. Standard error values are presented below mean concentrations for Land uses.

Element	Land use				International consensus-based ^a		Canada & BC ^b		Ontario ^c		Luoma & Rainbow (2008)
	F	A	M	C	TEC	PEC	ISQG	PEL	LEL	SEL	FAC
Metals											
As	9 ± 0.74	11 ± 0.57	15 ± 2.08	9 ± 1.52	9.79	33	5.9	17	6	33	–
Cd	0.8 ± 0.26	0.7 ± 0.06	0.6 ± 0.09	0.5 ± 0.09	0.99	4.98	0.6	3.5	0.6	10	–
Cr	67 ± 3.95	61 ± 2.19	48 ± 3.13	63 ± 4.30	43.4	111	37.3	90	26	110	–
Cu	147 ± 49.2	78 ± 9.23	116 ± 10.5	92 ± 17.4	31.6	149	35.7	197	16	110	–
Hg	0.22 ± 0.09	0.1 ± 0.02	0.16 ± 0.03	0.08 ± 0.01	0.18	1.06	0.17	0.486	0.2	2	–
Mn	740 ± 48.4	3584 ± 1737	1570 ± 195	1886 ± 424	–	–	–	–	460	1100	–
Ni	41 ± 2.64	43 ± 1.75	39 ± 7.45	39 ± 2.53	22.7	48.6	16 ^d	75 ^d	16	75	–
Pb	22 ± 6.75	14 ± 1.46	10 ± 0.66	10 ± 0.89	35.8	128	35	91	31	250	–
Se	2.0 ± 0.32	1.7 ± 0.07	3.1 ± 0.35	1.5 ± 0.07	–	–		2 ^e	–	–	2–4
Zn	262 ± 87.8	180 ± 54.4	144 ± 24.9	117 ± 14.7	121	459	123	315	120	820	–
Nutrients											
(Total) P	1077 ± 114	896 ± 18.5	1217 ± 89.3	950 ± 64.7	–	–	–	–	600	2000	–
n	14	16	15	11							

^a MacDonald *et al.* (2000).

^b CCME (2000); Nagpal *et al.* (2006)

^c Persaud *et al.* (1993)

^d Jaagumagi (1992): LEL and SEL for Ni based on screening level concentration (SLC).

^e Nagpal (2001).

The mean suspended sediment-associated metals and nutrient (i.e. P) levels for impacted (i.e. forestry, agriculture and mining) and control sites are presented in

Table 3.4. In most cases, average values for impacted sites are greater than mean values for the control sites. In some cases, mean values are noticeably greater, for example, As and Se for mining sites and Cu and Zn for forestry sites. As and Se are by-products of the Cu and Ag mining processes (Azcue *et al.*, 1995; Korte & Coulston, 1998), while Cu-rich local geology may have been disturbed and transported during forestry practices resulting in elevated levels for that land use (Hassan *et al.*, 2005). There is also a link presented in Christie & Fletcher (1999) between elevated Zn in sediments in harvested watersheds and culverts used in logging road construction, explaining the elevated concentrations recorded in this study. It should also be noted that some elements are elevated when compared with control values. This includes Pb for forestry, Mn for agriculture and Hg for forestry and mining. And, indeed, most geochemical concentrations from impacted sites are either similar or higher than concentrations measured at control sites.

Land use activities were also compared with SQGs. Generally, values are below upper threshold levels (e.g. PEC, PEL and SEL) for SQGs. Generally, the severe effect level (SEL) has the highest values of the SQGs presented in Table 3.4 and is therefore a good measure of the contaminated status of the collected sediment samples from the QRB. Values of Cu for forestry and mining sites, and Mn for agriculture, mining and control sites, however, exceed SEL thresholds (in bold, Table 3.4) and are thus of concern. The Se levels for sites impacted by mining are elevated and within the range cited in the literature for contaminated environments (Nagpal, 2001; Luoma & Rainbow, 2008). It is important to emphasize that the values for the QRB presented in Table 3.4 represent mean values for each land use activity and that some

individual samples were significantly greater than upper SQG levels, such as 31.1 $\mu\text{g g}^{-1}$ (As), 700 $\mu\text{g g}^{-1}$ (Cu), 5.7 $\mu\text{g g}^{-1}$ (Se) and 2509 $\mu\text{g g}^{-1}$ (P).

Table 3.5 Comparison of mean bed sediment contaminant concentrations ($\mu\text{g g}^{-1}$ dry weight) for land use activities (F, A, M, C) to sediment quality guidelines: TEC, threshold effect concentration; PEC, probable effect concentration; ISQG, interim sediment quality guidelines; PEL, probable effect level; LEL, lowest effect level; SEL, severe effect level; FAC, freshwater ambient criteria. Values in bold represent potentially toxic concentrations and are discussed in the text. Standard error values are presented below mean concentrations for Land uses.

Element	Land use				International consensus-based ^a		Canada & BC ^b		Ontario ^c		Luoma & Rainbow (2008)
	F	A	M	C	TEC	PEC	ISQG	PEL	LEL	SEL	FAC
Metals											
As	8 ± 0.27	12 ± 1.06	18 ± 3.83	7 ± 1.01	9.79	33	5.9	17	6	33	–
Cd	0.4 ± 0.03	1 ± 0.09	0.8 ± 0.12	1 ± 0.12	0.99	4.98	0.6	3.5	0.6	10	–
Cr	52 ± 1.28	53 ± 2.25	47 ± 3.53	42 ± 5.48	43.4	111	37.3	90	26	110	–
Cu	46 ± 3.85	55 ± 3.89	101 ± 16.2	88 ± 20.3	31.6	149	35.7	197	16	110	–
Hg	0.09 ± 0.01	0.08 ± 0.01	0.14 ± 0.03	0.08 ± 0.01	0.18	1.06	0.17	0.486	0.2	2	–
Mn	671 ± 66.0	1106 ± 184	806 ± 112	1636 ± 533	–	–	–	–	460	1100	–
Ni	42 ± 2.40	48 ± 2.67	39 ± 3.29	40 ± 1.09	22.7	48.6	16 ^d	75 ^d	16	75	–
Pb	6 ± 0.18	10 ± 0.81	9 ± 0.76	8 ± 1.16	35.8	128	35	91	31	250	–
Se	3.4 ± 0.30	4 ± 0.24	4.3 ± 0.38	3.5 ± 0.17	–	–		2 ^e	–	–	2–4
Zn	81 ± 4.93	97 ± 5.53	93 ± 6.73	96 ± 14.5	121	459	123	315	120	820	–
Nutrients											
(Total) P	1114 ± 11.4	1038 ± 14.9	1137 ± 81.5	1068 ± 58.2	–	–	–	–	600	2000	–
n	2	7	6	6							

^a MacDonald *et al.* (2000).

^b CCME (2000); Nagpal *et al.* (2006)

^c Persaud *et al.* (1993)

^d Jaagumagi (1992): LEL and SEL for Ni based on screening level concentration (SLC).

^e Nagpal (2001).

Mean bed sediment-associated contaminant concentrations, comparable to the suspended sediment values for each land use in Table 3.4, are presented in Table 3.5. As with the suspended sediment, most land use values are equal to or exceed control site values. Of greatest interest are values which exceed upper SQG thresholds and these include, As for mining (Canadian and BC SQGs only), Mn for agriculture and control, and Se for agriculture and mining (in bold, Table 3.5). Compared to suspended sediment, bed sediment values displayed a higher proportion of mean concentrations exceeding lower SQG thresholds (i.e. TEC, ISQG and LEL); for example, As, Cu, Mn, Ni, Se, and total P for all land uses, Cr for forestry, agriculture, and mining sites, and Cd for agriculture, mining, and control sites. Falling below SQG contamination thresholds for all land uses are Hg, Pb, and Zn. However, individual samples have higher values, sometimes exceeding lower SQG thresholds (i.e. $0.36 \mu\text{g g}^{-1}$ (Hg for site M1) and $167 \mu\text{g g}^{-1}$ (Zn for site C1)). Comparison of the concentrations for the five COIs for the suspended and channel bed sediment samples from the four land uses (A, F, M and C) are presented in Appendix A2.

Although some mean values listed in Tables 3.4 and 3.5 are relatively high and identified here as *of concern*, it should be recognized that such elevated values do not necessarily mean that these metals and nutrients are toxic to aquatic ecosystems and detrimental to human health. The values presented represent totals and research (e.g. Stone & Droppo, 1996; Carter *et al.*, 2006) has shown that a significant portion may not be bioavailable (i.e. not easily available for uptake or use by organisms). Thus, comparison of total values of metals and nutrients with SQGs should be treated with some caution. It is arguable that information on metal and nutrient speciation would be more informative for identifying risk to aquatic organisms and

human health. For example, Cu and Zn bioavailability has been shown to be strongly dependent on pH and organic carbon content (Álvarez *et al.*, 2003). Therefore, seasonal variability of Zn and Cu biological potency may be expected. In the QRB, such organic material influxes occur during freshet and storm events, and the post-spawning period of salmon populations (Rex & Petticrew, 2008; Petticrew & Albers, 2010).

3.4 Conclusions

Fine-grained suspended and bed sediment was collected from streams draining different land use activities in the QRB. Mean land use values exceed all three geological baselines with few exceptions, suggesting that land use-associated impacts play a larger role in fine sediment contaminant concentrations in the QRB than background geology.

Generally, metal and nutrient concentrations for impacted sites (i.e. agriculture, forestry and mining) were greater than for control sites. Suspended sediment values of As, Cu and Mn for mining sites, Cu and Zn for forestry sites, and Mn for agriculture sites were close to or exceeded upper SQG thresholds and may be of concern. Furthermore, Se levels for sites impacted by mining were also elevated. The results suggest that metal mining and to some extent forest harvesting are having a greater influence on the concentration of sediment-associated metals and nutrients in the QRB than agricultural activities.

For bed sediment, mining also exceeded upper SQG thresholds (e.g. As and Se) and appears influential on QRB contaminant concentration levels. However, agriculture also exceeded upper threshold values (e.g. Mn and Se), and displays a greater impact than forestry. Overall, bed sediment had a higher proportion of lower SQG

threshold exceeding values in comparison to suspended sediment results. Therefore, a slightly larger proportion of potentially toxic sediment may exist as bed sediment in the QRB.

The health of the QRB as a function of fine sediment quality is difficult to determine, however, it is possible to state that pockets of land use-associated contamination do exist for certain metals and nutrients.

CHAPTER 4: TEMPORAL AND SPATIAL VARIATIONS IN SEDIMENT-ASSOCIATED METALS AND P

4.1 Introduction

The prime focus of this chapter is to identify and attempt to explain the temporal and spatial differences in the metal and P content of the sediment within the QRB during the 2008 field season (i.e. research objective 2, see section 1.2). A secondary goal is to begin the process of creating a multi-property signature (Collins *et al.*, 1998; Walling *et al.*, 1999) capable of differentiating between the four main land use influences (agriculture, forestry, mining and control/anthropogenically unmodified) found in the QRB. The outcomes of this latter goal, and its application to the definition of the QRB-scale signature, through a bottom-up (source ascription) method, will be explored further in Chapter 5 (i.e. research objective 3, see section 1.2).

Geochemical concentration data analyzed in Chapter 3 were not corrected for differences in particle size composition. This enabled comparisons with SQGs and other reference guidelines, which also contained uncorrected values. However, a particle size correction is applicable in this chapter, as justified below, and a well-established method utilized in similar studies (e.g. Collins *et al.*, 1997b; Carter *et al.*, 2003; Walling *et al.*, 2008) has been used. The method accounts for variations in particle size composition via the specific surface area of the samples and the associated number of potential sorption sites. A preferential association between most geochemical elements in the fluvial system and fine-grained sediment has been well documented (e.g. Horowitz, 1991; Owens & Walling, 2002). The general trend is an increase in elemental concentration associated with an increase in the number of po-

tential sorption sites. This equates to geochemical concentration increases with decreasing particle size (or with increasing specific surface area).

In the fluvial environment, fine-grained sediment is selectively mobilized and transported, while coarser sediment is preferentially deposited (Walling *et al.*, 2000). The grain size distribution of the suspended load is further influenced by variations in flow regime, the characteristics of source materials, and sediment storage and remobilisation, amongst other things (Horowitz, 1985; Church & Hassan, 2002). Hence, it is expected that grain size composition will differ both spatially and temporally between the various sampling sites investigated in the QRB. Therefore, in the interest of limiting grain size-related variations, a particle size correction factor was applied to the raw QRB sediment geochemical data.

Both temporal and spatial variations in contaminant concentrations of transported river sediment can be influenced by land use-specific inputs (e.g. acid mine drainage for mining (Protano & Riccobono, 2002), fertilizers for agriculture (Gimeno-García *et al.*, 1996)). Temporal variations are likely to be a function of three factors: (i) variations in source inputs and delivery; (ii) variations in transport conditions (i.e. rainfall, snowmelt and river discharge); and (iii) variations in sediment-contaminant sorption/desorption behaviour (e.g. due to changes in pH, redox, organic matter content, particle size) (Horowitz, 1985). Due to the scope of this project, in this chapter (i) and (ii) were addressed while the importance of (iii) was noted and discussed (see section 1.1) but not directly addressed in the analysis, with the exception of the particle size correction.

Spatial variations can be the result of any of the above factors measured at a given point in time for a predetermined spatial area. Here, spatial variation analysis compares and contrasts each land use-associated sub-basin (spatial area of interest)

during the entire sampling season (set point in time). The conclusions drawn from this chapter characterize sediment-associated contaminant concentrations in the QRB over space and time for the 2008 field season.

4.2 Methods

In order to satisfy the primary goal of this chapter and research objective 2 (see section 1.2), while limiting the analysis to geochemical elements thought to be of interest for sediment contamination in the QRB, the most prominent land use-associated geochemical elements were selected. In Chapter 3 (see section 3.3.2), As, Cu and Mn for mining; Cu and Zn for forestry; and Mn for agriculture, were close to or exceeded upper Sediment Quality Guideline (SQG) thresholds for suspended sediments. Se levels also appeared elevated for mine sites and were suspected to be local sources of contamination. For bed sediment, As and Se for mining, and Mn and Se for agriculture, exceeded upper SQG thresholds. Therefore As, Cu, Mn, Se and Zn concentration values were used in temporal and spatial variation analysis. Spatially, the five contaminants of interest (COI) were compared and contrasted by land use with each other using summative statistics (e.g. mean, maximum, and minimum values). Temporally, the COI were compared to corresponding precipitation (PPT) and discharge (Q) values using GraphPad Prism 5 for Mac OS X (GraphPad, 2010). The meteorological station at the Quesnel Airport (53°01'34" N, 122°30'37" W) provided daily precipitation data (Environment Canada, 2011). Hydrometric data was gathered from the Water Survey of Canada (WSC) gauging station at Penfold Creek (52°47'29" N, 120°44'54" W) (WSC, 2011). Of the available gauging stations in the basin that at Penfold Creek was deemed the most appropriate with QRB sampling lo-

cations in terms of sub-basin size and mean annual discharge (i.e. 199 km² and 4.7 m³s⁻¹, respectively, for Penfold Creek (Rood & Hamilton, 1995)).

The secondary goal of this chapter was to begin the creation of a multi-property signature capable of distinguishing between land use types. In this process, the relative toxicity of a given geochemical is not relevant. Therefore, all 32 geochemical elements are incorporated into the analysis using rank sum tests.

4.2.1 Sediment collection and analysis

The field and laboratory methods used, from sample collection to determination of elemental concentrations, have been described in Chapter 3 (see section 3.2). Briefly, suspended and bed sediment samples were collected from 13 sites within the QRB using the Phillips sampler (Phillips *et al.*, 2000) and a re-suspension method (Lambert & Walling, 1988; Walsh *et al.*, 2007), respectively.

In the laboratory, a range of base cations, heavy and trace metals, and nutrients, totaling 32 geochemical properties, were selected for analysis (i.e. Al, Sb, As, Ba, Be, Bi, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Hg, Mo, Ni, P, K, Se, Si, Ag, Na, Sr, Sn, Ti, U, V, Zn and Zr). Samples underwent acid and microwave digestion using nitric and hydrochloric acids. Concentrations of these fine sediment-associated geochemical properties were then determined using ICP-MS at UNBC.

4.2.2 Particle size correction

Particle size analysis was conducted using a Malvern Multisizer Hydro 2000G at Simon Fraser University, B.C. (also see section 2.2.4). The specific surface areas and geochemical concentrations of each sample were used to make corrections for differ-

ences in particle size composition between samples and sites using Eq. (4.1) (Russell *et al.*, 2001):

$$C_c = (S_x / S_s)C \quad (4.1)$$

where C is the measured property concentration in a sediment sample from a land use (e.g. F, A, C), C_c the property concentration corrected for particle size, in order to be directly comparable with the value for suspended sediment, S_x is the mean specific surface area of suspended sediment representing the control, and S_s is the specific surface area of the sample to be corrected.

4.2.3 Carbon and Nitrogen

An additional correction is sometimes made for organic matter content, based on the contaminant sorption ability of organic matter when attached to or incorporated within suspended sediment particles (Yin *et al.*, 2002). Some studies make this correction using organic carbon (C) content (e.g. Collins *et al.*, 1997b) in an attempt to further enhance comparability between sediment and potential sources. Others (e.g. Walling *et al.*, 1999; Martinez-Carreras *et al.*, 2010) suggest that this could result in overcorrection, citing that the science behind organic matter influence on contaminant concentration is not as well understood as that of particle size variation. I have agreed with the argument against potential overcorrection and decided not to include an organic matter correction.

4.2.4 Statistical analysis

Spatial variability was tested using two rank sum tests. The Kruskal-Wallis *H*-test (K-W test) (three or more potential geochemical signature properties) and Mann-Whitney *U*-test (M-W test) (two potential geochemical signature properties) were utilized to quantify the statistical significance of variability between and within QRB land uses. All rank sum tests were conducted using R 2.12.1 (2010).

Strong confirmation of a geochemical property's ability to discern between land use-specific material is required before that property can be incorporated into an effective multi-component signature (Carter *et al.*, 2003). Since fingerprint or signature data uncommonly satisfy the conditions required for parametric distributions (i.e. normal distribution of the data and equal variances) (c.f. Collins *et al.*, 1998), a non-parametric test was an appropriate choice for these data. Additionally, it was decided in this situation to use the well-established statistical protocols developed and practiced by others for developing distinct geochemical signatures as part of sediment fingerprinting (e.g. Collins *et al.*, 1996; 1997a; 1997b; Russell *et al.*, 2001).

The non-parametric K-W test was used to test the ability of all potential signature properties to distinguish between and within the land use-specific sub-basins (Crawley, 2007). The test is well suited for the relatively small QRB material datasets due to its assumption of non-parametric data and power of 95% (i.e. $P=0.05$) (Hammond & McCullagh, 1978). Here, the hypothesis tested by the K-W test was:

- H^0 : *the measurements of the geochemical property exhibit no significant differences between land uses.*
- H^a : *the measurements of the geochemical property exhibit significant differences between the land uses.*

The critical H value was 7.815 for inter-land use variability and 5.991 for intra-land use variability. In distributions with more than three groups (i.e. land uses in the QRB dataset), critical H values are not available and it is suggested that analogous X^2 (Chi-Square) values be substituted into the analysis (Kruskal & Wallis, 1952). It should be noted that the test is applied to the values of a given geochemical property across the entire dataset (i.e. all land use types). Therefore, resulting H values greater than the critical H value, confirm inter-category contrasts, rather than variability between all possible pairs of source categories (Fowler & Cohen, 1990).

Analysis of variance between two land uses required the non-parametric M-W test (analogous to the Wilcoxon rank sum test). In this analysis the medians of two samples from the same distribution are tested for equivalence (Wilcoxon, 1945). A P -value and U -value are given for each paring in the test. The U -value is equal to the number of pairs with (agriculture, A; forestry, F; mining, M) < C (control/reference) (Milton, 1964). U -values above a higher threshold value suggest a significantly greater number of parings with higher values for C compared to land use values. The inverse is true for all U -values below a lower threshold. The difference between all values outside the range of the upper and lower thresholds is deemed statistically significant. This is confirmed by the P -value. Both thresholds can be determined using the charts presented in Milton (1964). For the QRB the hypothesis tested by the Mann-Whitney U -test was:

H^0 : *the underlying distributions of geochemical property x in land use group 1 (either F, A, or M) and land use group 2 (C) are equal.*

H^a : *the underlying distributions of geochemical property x in land use group 1 and land use group 2 are shifted (i.e. they have different medians).*

The P -value was set at 0.05, allowing all properties with P -values greater than the critical value to be discarded. All properties accepted by the critical value therefore rejected the null hypothesis and displayed significant variability in medians.

4.3 Results and discussion

4.3.1 Temporal inter-land use variations

In this study, monthly samples were collected over six, month-long, sampling periods; individual intra-storm samples were not collected. Thus, temporal variation was investigated monthly, revealing seasonal high and low flow conditions, but not distinguishing storm events from other causes of sediment introduction to the river. Total monthly discharge values were used to distinguish between high and low flow conditions. The total monthly discharge and precipitation patterns, recorded at the Quesnel Airport meteorological station and the Water Survey of Canada gauging station at Penfold Creek during the sampling period, are presented in Figure 4.1 and associated with their respective sampling periods in Table 4.1. For the QRB, the April-May (A-M) and May-June (M-J) sampling periods (i.e. periods during which the sampler collected sediment) represent high flow conditions during the spring freshet. August-September (A-S) and September-October (S-O) represent low flow conditions during late summer and early fall, but are influenced by short-duration rain storm events that cause higher flows. In the interim period, June-July (J-J) and July-August (J-A), is when snowmelt-dominated freshet and late-summer precipitation events intersect.

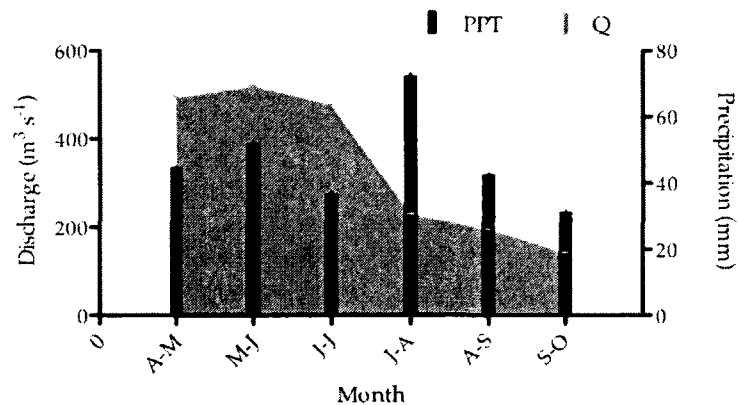


Fig. 4.1 Total monthly precipitation (PPT) and discharge (Q) values. Values were recorded during the 2008 field season at the Quesnel Airport meteorological station (Environment Canada, 2011) and a Water Survey of Canada gauging station at Penfold Creek (WSC, 2010).

Table 4.1 Sampling schedule and associated total PPT (measured daily) and total Q during sampling periods, with standard error in parentheses. Dates at either end of sample periods represent both sampler installment and sediment retrieval, with the exceptions of April 29th (i.e. initial deployment) and October 24th (i.e. final sampler emptying and removal).

Sample period (2008)	Total PPT (mm)	Total Q ($\text{m}^3 \text{s}^{-1}$)
April 29 th – May 30 th	44.7 (± 0.4)	494.1 (± 2.1)
May 30 th – June 25 th	52.0 (± 0.6)	520.9 (± 0.9)
June 25 th – July 28 th	36.6 (± 0.6)	477.6 (± 1.1)
July 28 th – August 24 th	72.3 (± 0.9)	230.0 (± 0.5)
August 24 th – September 24 th	42.6 (± 0.4)	195.3 (± 0.5)
September 24 th – October 24 th	31.2 (± 0.4)	143.3 (± 0.2)

Total monthly discharge values rose to peak levels through the spring months ($520.9 \text{ m}^3 \text{s}^{-1}$ for M-J), decreased steadily through the summer months, and decreased more gradually during the fall months (i.e. $195.3 \text{ m}^3 \text{s}^{-1}$ and $143.3 \text{ m}^3 \text{s}^{-1}$ total discharge for A-S and S-O, respectively). The pattern for total precipitation during each sampling period contained greater fluctuation than discharge. Early spring rains and late-summer storm events accounted for high values in A-M (44.7 mm/month), M-J (52.0 mm) and J-A (72.3 mm). Seasonal precipitation dips occurred in J-J (36.6 mm) and S-O (31.2 mm).

Figure 4.2 presents temporal patterns for As, Cu, Mn, Se and Zn concentrations of suspended sediment for each land use type to highlight inter-land use differences.

For As, mining values were elevated compared to other land use types for most sample periods. The mining signature was high during M-J, compared to most other sample periods, while the other land use types were similar to the preceding period (i.e. A-M). Since mean PPT decreased during this period it is likely that point source inputs associated with mining activities were important. Conversely, in J-J, As concentrations at agriculture, forested and control sites were higher, which coincided with an increase in precipitation, suggesting the importance of diffuse sources for these land uses. There was also a noticeable agricultural signature increase from J-J to J-A accompanied by the highest precipitation values. Again, this suggests a link between PPT and surficial sediment mobilization from diffuse sources. In S-O, despite low flow conditions, As concentrations at the mining sites were elevated, suggesting that there was an influx of As-associated sediment due to mining operations, which are independent of PPT and Q.

In Chapter 3 (see section 3.3.2) Cu was linked to mining and forestry activity. Through A-M and M-J, Cu values were broadly similar for all land use types. In J-J, there was a spike from forestry as precipitation increased and the snowmelt-induced discharge began to decrease. Forestry concentrations remained high throughout J-A. During this period, the remaining land use types showed lower fluctuation. This is of particular interest for mining, which remained near $100 \mu\text{g g}^{-1}$ for all sample periods (i.e. did not fluctuate over time even though site M1 was an active copper mine). Of note are the elevated Cu values for control during the period with lowest PPT and low Q values in A-S. This suggests a more pronounced background geochemistry (maybe reflecting dissolved inputs from groundwater which subsequently binds to sediment) during low flow conditions, as found in Kimball *et al.* (2002) and Mayes *et al.* (2008).

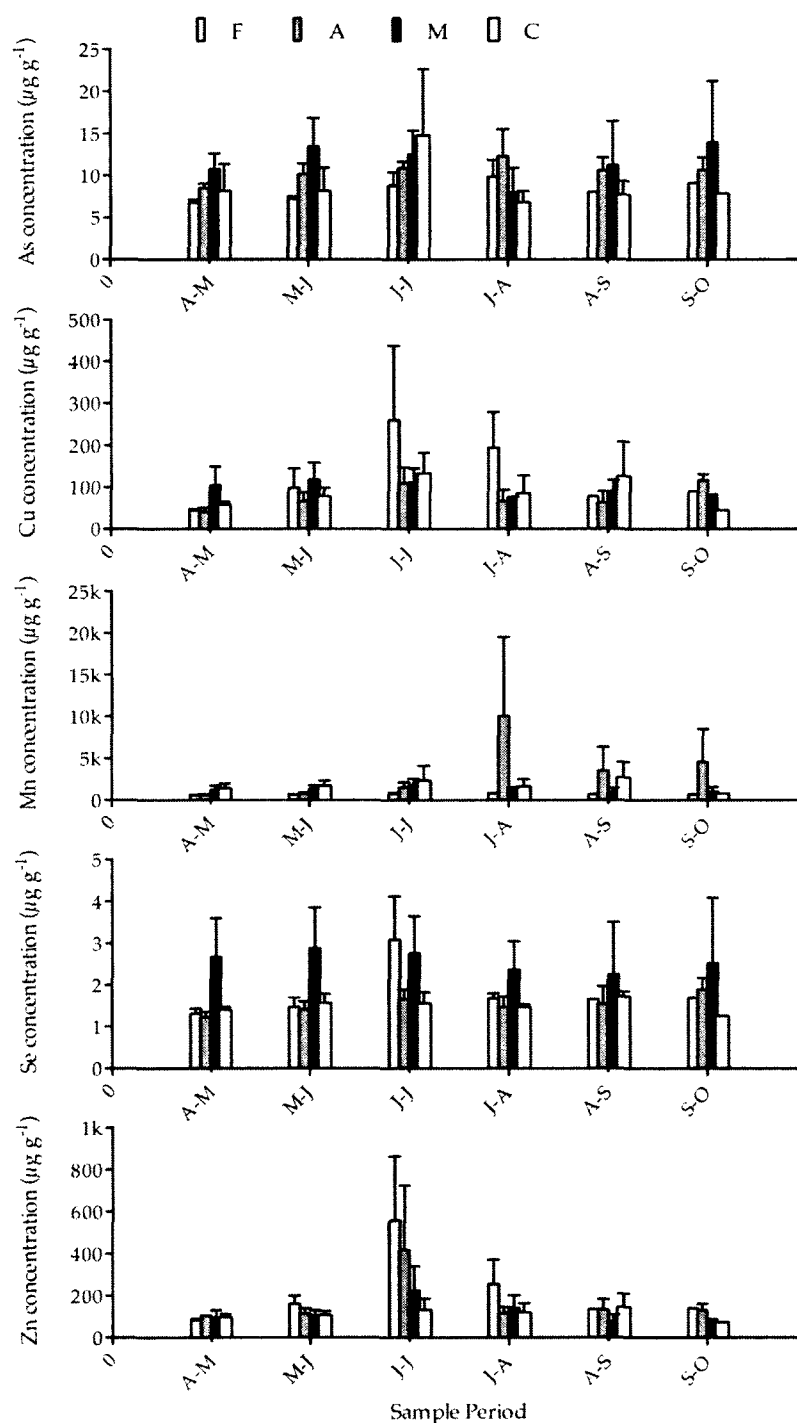


Fig. 4.2 Temporal pattern of suspended sediment-associated geochemical concentrations (As, Cu, Mn, Se, and Zn), displayed by land use type and sample period (monthly). Land use types include: forestry (F), agriculture (A), mining (M), and control (C).

Of the five COI, Mn is arguably the most unique. Geochemical concentrations were low and of a similar pattern for all land uses during the freshet and into the summer (i.e. A-M, M-J, and J-J) and appeared equally affected by changes in Q and PPT. However, in J-A there was a distinct spike, up to $12000 \mu\text{g g}^{-1}$, from agriculture, while all values for other land uses at this time remained around $2000 \mu\text{g g}^{-1}$ ($\sim 10000 \mu\text{g g}^{-1}$ less than agriculture). This increase was so drastic, and so specific to one land use type, that its validity is suspicious, although values were also relatively high in subsequent months (i.e. A-S and S-O). However, there was no marked event during fieldwork or subsequent lab analysis that would indicate that the concentration was false. This spike in agricultural input occurred during a period of high PPT. It may be due to the application of fertilizers, and associated impurities, or the activity of livestock at pasture in conjunction with heavy rainfall (Gimeno-García *et al.*, 1996; Taylor *et al.*, 2008). Also of note is the temporal pattern for control, which is similar to that for Cu, where geochemical values were level for all months with one exception, A-S, when Mn levels were high even though values for PPT and Q were low.

For Se there was a consistently elevated signature from mining throughout the field season, which agreed with results in Chapter 3 (see section 3.3.2). Here the pattern was similar to As, where mining has the highest geochemical concentration and does not appear to be altered by changes in PPT or Q over time. Additionally, the forestry-associated pattern for Cu, Se and Zn, had a reoccurring theme during J-J. Here, the forestry signature was elevated compared to other forestry values, and often double that of all other months. This pattern may be the result of melt-water flowing over frozen soil during M-J, contributing to lower sediment delivery (McDonald & Lamoureux, 2009). During the highest precipitation period in J-A, much of the winter snowpack had already melted and mean Q had decreased sig-

nificantly. Thus, QRB soils were capable of absorbing much of the rainfall without oversaturation and subsequent sediment release (Goodwin *et al.*, 2003). During J-J, when Q was still high and PPT was increasing, diffuse land uses (such as agriculture and forestry) likely became oversaturated and released their largest surficial sediment and sediment-associated geochemical loads.

As mentioned above, there was a large influx of Zn from forestry during J-J. From M-J to J-J the forestry-associated Zn concentration rose from $162.03 \mu\text{g g}^{-1}$ to $559.03 \mu\text{g g}^{-1}$. Christie & Fletcher (1999) link contamination of forestry sediments by Zn to culverts used in road construction. However, there was also a pronounced input from agriculture in J-J, adding further support to the theory that precipitation patterns and changes in soil water content caused increased Zn inputs. However, both forestry and agriculture spikes could also be explained by increased tree harvesting and livestock activity during this time, respectively. Regardless of the cause, be it natural, a function of land use practices, or a combination of both, elevated Zn concentrations in J-J for forestry and agriculture were the most prominent aspects of the Zn temporal pattern.

When all five COI are examined, some general trends in temporal inter-land use variation emerged. For As and Se, there was evidence to suggest that the mining signature reacted like an anthropogenically influenced point source, which fluctuated independently of PPT or Q trends. With Cu, Se, and Zn, forestry (and agriculture for Zn) are substantially elevated during J-J, suggesting oversaturation of the soil and subsequent sediment load transport in concert with increased seasonal harvesting activity. Finally, agriculture had high concentrations of Mn, which were six times higher than any other land use during J-A. This may be the result of seasonal fertilizer use or livestock activity, particularly in the riparian zone. Analysis of site-

specific temporal variations is an important next step in determining the cause of inter-land use variations, by identifying the differences within land use types.

4.3.2 Temporal intra-land use variations

The temporal profiles comparing suspended sediment-associated Mn, Se and Zn concentrations for each site within each disturbed land use (i.e. F, A, and M), and PPT and Q trends, are presented in Figures 4.3-4.5. Trends for control sites were omitted, as there was comparatively little variation during the 2008 field season. Profiles for As and Cu, although not shown due to the similarity of patterns with other COI, are discussed near the end of this section.

In Figure 4.3, Mn values during A-M and M-J were fairly similar for forestry, at approximately $500 \mu\text{g g}^{-1}$ for all three sites. However, in J-J, F2 and F3 remained unchanged while F1 showed an increase to $1061 \mu\text{g g}^{-1}$. The F1 signature then decreased in J-A, while both F2 and F3 showed a slight increase. It should be noted that the streams feeding F1 and F3 dried up by August, leaving only site F2 during A-S and S-O. As discussed in section 4.3.1, the F1 spike in J-J was likely the result of an over-saturation of the soil, possibly in concert with increased tree harvesting activity. The comparatively high values of F2 and F3 in J-A coincided with peak PPT values and may have resulted from PPT-induced erosion and subsequent transport. These temporal differences could be either due to specific harvesting practices at site F1 or differences in sediment delivery.

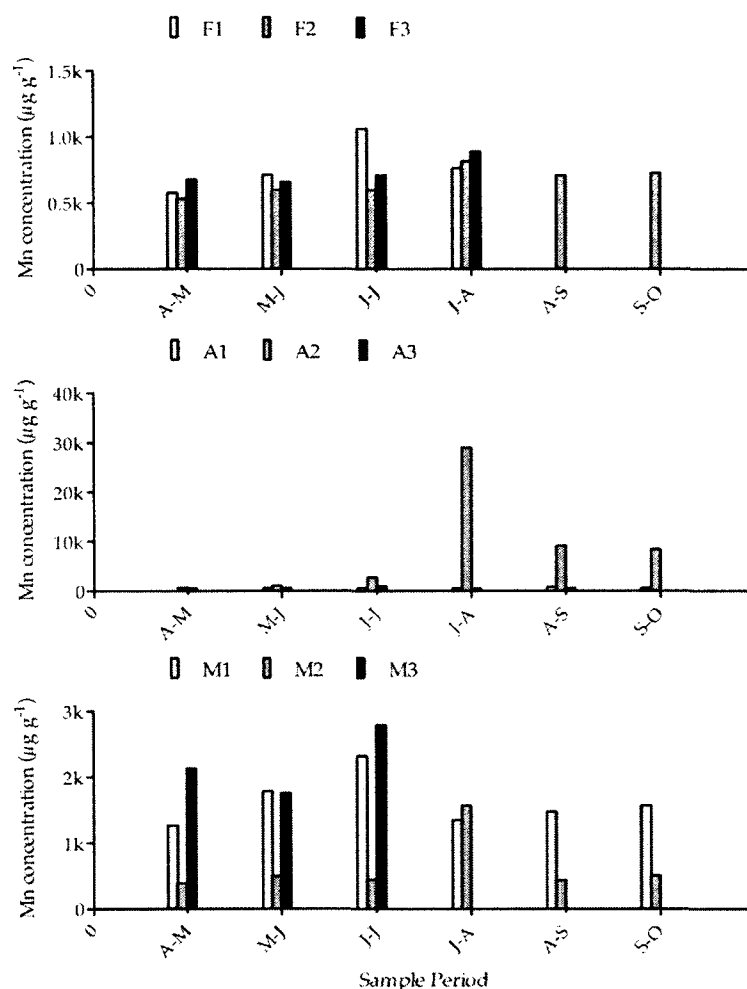


Fig. 4.3 Temporal pattern of suspended sediment-associated Mn concentration values for each land use type and sample period (monthly). Land use types include: forestry (F1-F3), agriculture (A1-A3), and mining (M1-M3).

The link between agriculture and elevated Mn, first revealed in Chapter 3 (see section 3.3.2), can now be further delineated by sample site. A2 stood out as having the highest Mn values, while A1 and A3 remained low throughout the field season. With site A2, as precipitation increased from J-J to J-A, there was an increase from $2811 \mu\text{g g}^{-1}$ to $29,009 \mu\text{g g}^{-1}$. The J-A value coincided with peak PPT. A2 values also remain high in A-S and S-O, but were 1/3 that of J-A. Overall, elevated Mn values

for A2 appeared related to precipitation, but were more likely the result of livestock activity and/or fertilizer use during this time.

Prior to discussing the results for mining for Mn, it is important to note that some sample periods were not represented due to seasonal drought. Specifically, no samples were collected for site M3 (the active gold mine) from J-J to S-O. M3, however, did show elevated values and seemed to follow the PPT trend over that of Q, from A-M to J-J. Values from M1 (the active copper mine) were also elevated compared to M2 during most sample periods. As with site M3, the highest values for M1 occur in J-J, but the similarities between sites ended there. Unlike M3, M1 did not appear to follow the PPT trend or the Q trend and was more likely the result of variations in mining activity. M2 (the inactive Bullion Pit mine) appeared to react to the late summer storm events represented by peak PPT in J-A. In that sample period M2 increased from its relatively stable baseline of $\sim 450 \mu\text{g g}^{-1}$ up to $1568 \mu\text{g g}^{-1}$. This suggests a link between the open canyon of the inactive mine and the erosive ability of PPT events.

The intra-land use temporal patterns for suspended sediment-associated Se concentrations in the QRB are presented in Figure 4.4.. For the forestry sites, site F1 stood out. There was a sharp increase and a sharp decrease in Se concentration on either side of the J-J period. For example, between M-J and J-J, the F1 signature increased from $1.92 \mu\text{g g}^{-1}$ to $4.97 \mu\text{g g}^{-1}$. The F3 value was also elevated in J-J. Both F1 and F3 temporal trends were possibly due to a period of over saturation of their respective soils at the point when the recently thawed ground received increasing PPT and the remnants of winter snowmelt. Interestingly, the F2 signal remained relatively constant from A-M to S-O and did not increase during J-J with the other two sites. This was perhaps due to less recent harvesting activity in the sub-basin or

greater barriers to sediment entry into the stream and hence sediment deposition and storage.

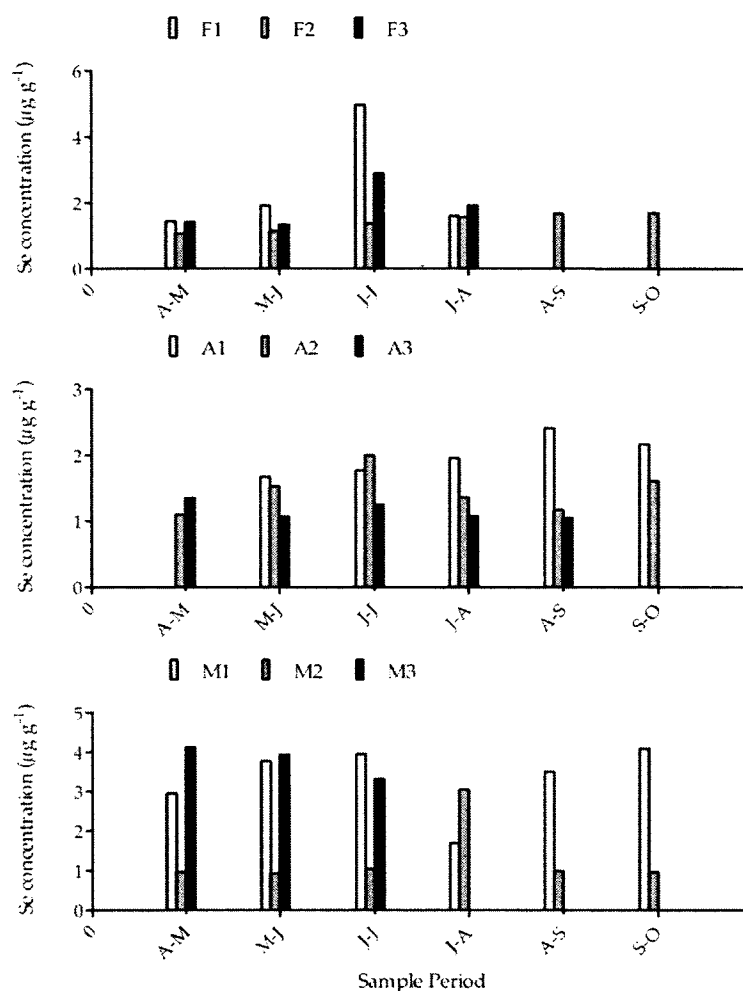


Fig. 4.4 Temporal patterns of suspended sediment-associated Se concentration values for each land use type and sample period (monthly). Land use types include: forestry (F1-F3), agriculture (A1-A3), and mining (M1-M3).

Agricultural land use is a diffuse source of sediment and COIs in the QRB. As such, PPT is often a strong mechanism of agricultural sediment transport. Se concentrations for sites A1, A2, and A3 all appeared to fluctuate with PPT levels to varying degrees, particularly between A-M and J-J. Between J-A and S-O, this pattern was less consistent, and in the case of A1, was actually counter to the PPT trend. A possi-

ble explanation for this was seasonal variations in vegetation, specifically grass for cattle grazing. During A-M to J-J the grass cover may be less extensive and the soil oversaturated and muddy, promoting sediment mobilization and delivery to the river. By J-A, vegetation cover may be dense enough to reduce surface erosion and may retain any mobilized sediment, even during intense, late summer storm events. By A-S and S-O, much of the grass will have been consumed by livestock or slowed in growth rate, again becoming less dense and resulting in elevated sediment erosion and transport. The agriculture-associated Se was likely from impurities in fertilizers used to promote grass growth, which was thus available for transport of contaminants attached to fine-grained sediment, such as Se.

The trends for mining sites for Se were very similar to those observed for Mn. Again, values for M1 fluctuated independently of PPT and Q patterns, and M2 spiked only during peak PPT in J-A. This time, however, M3 was influenced less by PPT and appeared to decrease in J-J as Q decreased. Both M1 and M3 were elevated compared to M2 in most sample periods, suggesting that Se was a waste product of the active mining processes for Cu and Au (i.e. M1 and M3 respectively) (e.g. Luoma & Rainbow, 2008). However, the Se increase for M2 in J-A (the period with highest precipitation) suggested that Se may also have occurred in high concentrations in sediment on the inactive hillslopes of the Bullion Pit, but required significant rainfall to be mobilized and enter the fluvial system.

The intra-land use temporal variation patterns for Zn are presented in Figure 4.5. The elevated values in J-J, a prominent trend for all three land uses, were attributed to a single site for each land use.

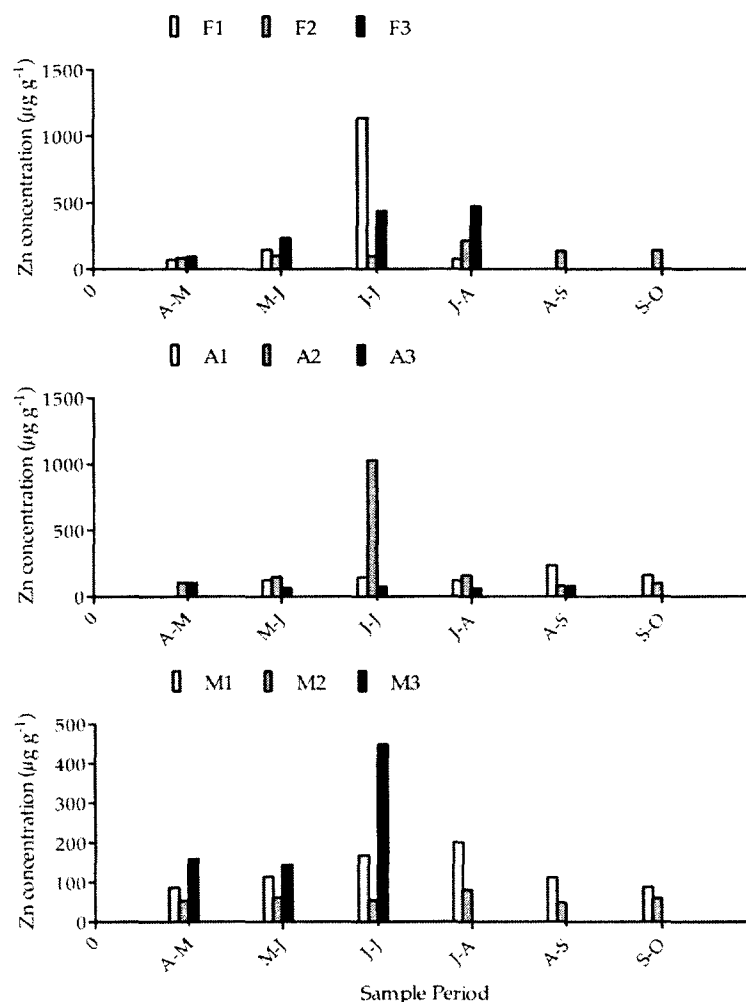


Fig. 4.5 Temporal patterns of suspended sediment-associated Zn concentration values for each land use type and sample period (monthly). Land use types include: forestry (F1-F3), agriculture (A1-A3), and mining (M1-M3).

For forestry, site F1 stood out, and was $698 \mu\text{g g}^{-1}$ greater than the next closest forestry site (i.e. F3) in J-J. However, the F1 signature was low for all other sample periods ($\sim 100 \mu\text{g g}^{-1}$). This pattern was consistent for F1 for both Mn and Se. Mirroring the F1 spike in J-J were sites A2 and M3. In agriculture, A2 was the only site to display significant temporal variation. For mining, site M3 appeared to follow the PPT trend from A-M to J-J, but the increase in Zn concentration was disproportionate to the PPT increase. For all three elevated sites in J-J, it was possible that a com-

ination of increased PPT, recently thawed soil, and continued snowmelt, culminated in ideal conditions for sediment transport into the fluvial system, although the reason that not all sites were affected at this time was uncertain, which may also reflect site-specific conditions and land management operations.

In summary, considering all COIs, temporal trends for As and Cu are not shown but are discussed here. Forestry values for both COI were comparable to each other and those already displayed for Se and Zn. In all cases, site F1 was elevated compared to F2 and F3, particularly during J-J. This also applied to As, where F1 was also high during peak PPT in J-A. For agriculture, sites A1 and A2 were elevated relative to A3 and appeared to follow the PPT trend. The mining trends for As and Cu were both similar to Se for M3, which was elevated during A-M to J-J. However, for As, site M2 also stood out and appeared to follow the Q pattern from A-M to J-A and then the PPT pattern from A-S to S-O.

In general, strong temporal links existed between diffuse contaminant sources (e.g. F1, A2, M2) and precipitation, which were both elevated during J-J and J-A. Point source contributions from M1 appeared to be independent of either PPT or Q temporal patterns and were possibly an artifact of mine activity rather than natural introduction. These results concur with previous work comparing diffuse and non-diffuse sediment-associated geochemical sources (e.g. Horowitz, 2009). Some temporal intra-land use variation may also have been due to unique PPT, Q, and seasonal thaw conditions during J-J, which induced substantial sediment-associated geochemical delivery for select sites (e.g. F1 for Cu, Mn, Se and Zn; A2 for Cu and Zn; M3 for Zn). Finally, the spike in Mn for agriculture was attributed to site A2 and occurred in concert with peak PPT values.

4.3.3 Spatial inter-land use variation

In the QRB, forestry, agriculture (with some potential scale-based exceptions mentioned in section 1.1.4), and control land uses are diffuse sources, while mining sites are point sources (with the arguable exception of site M2, The Bullion Pit). This distinction is important when considering sources of spatial variation. That is, inputs from diffuse sources are greater with high precipitation and discharge, while point source inputs are generally independent of precipitation but are dependent on land use practice (Horowitz, 2009). By investigating spatial variation in the QRB, land use- and site-specific fluctuations in contaminant concentrations can be identified, analyzed, and linked to driving factors.

The five COI identified in section 3.3.2 are presented in Table 4.2, with each land use type being represented by combined values for all sample sites of that land use type. Forestry has the highest mean value for Cu and Zn, agriculture is elevated for Mn, and mining has the highest values for As and Se. Notable maximum values for individual samples are also presented and have contributed strongly to spatial and temporal variations: namely, 29,009 $\mu\text{g g}^{-1}$ Mn from A2 in J-A. Despite obvious spatial differences, when all four land use types are compared, none of the COI show statistically significant spatial variability according to rank sum testing.

Table 4.2 Mean suspended sediment-associated values for contaminants of interest (As, Cu, Mn, Se, and Zn) for forestry (F), agriculture (A), and mining (M) land use activities. Minimum and maximum values are presented in parentheses and n = number of samples from each land use type. Geochemical concentrations are particle size corrected.

Element	Concentration ($\mu\text{g g}^{-1}$)			
	F	A	M	C
As	8.26 (6.16 - 13.86)	10.66 (7.54 - 18.34)	11.78 (5.06 - 21.25)	9.01 (4.91 - 22.69)
Cu	140.5 (39.99 - 611.3)	77.31 (28.40 - 151.5)	99.21 (46.54 - 197.4)	91.97 (42.45 - 208.4)
Mn	717.9 (535.9 - 1061)	3638 (523 - 29,009)	1353 (389.0 - 2786)	1886 (612.9 - 4617)
Se	1.86 (1.06 - 4.97)	1.53 (1.05 - 2.41)	2.62 (0.93 - 4.13)	1.52 (1.26 - 1.85)
Zn	247.4 (71.83 - 1137)	177.2 (66.65 - 1030)	126.1 (49.69 - 450.2)	117.4 (75.35 - 210.2)
n	14	16	15	11

The results of the K-W tests and M-W tests identify geochemical elements with statistically significant variation between one or more land uses (i.e. not necessarily differences between all land uses). Comparing all land use types (F, A, M, C) gives an overview of spatial variation, while comparison of each individual anthropogenic land use (F, A, M) to control values, highlights differences between impacted and relatively undisturbed sites. When all land uses are compared (i.e. the K-W test) just over half of the geochemical properties tested show significant spatial variability (Figure 4.6). That is 17 of 32 properties produce test statistics in excess of the critical value (i.e. 7.815), indicating that there is a significant difference between one or more of the land use types for that geochemical property (Table 4.3). Also presented in Figure 4.6 are M-W test results comparing F, A and M to C individually. Additional K-W test result tables for intra-land use comparisons and M-W test result tables comparing F, A and M to C, individually, are presented in Appendix A2. It should be noted that the results of the K-W and M-W tests represent statistically determined

differences between land uses, but the elements selected by the tests do not necessarily make sense from a geochemical perspective. That is, there is no physical or geochemical basis for many of the 17 properties that passed the rank sum tests. For this reason individual M-W tests (e.g. between land uses and control values) and box-whisker plots may be more useful in revealing the comparative geochemical signatures of land uses in the QRB. Despite the above comments, the results of the K-W test on intra-land use comparisons are useful to this study when entered into the multivariate mixing model used in Chapter 5.

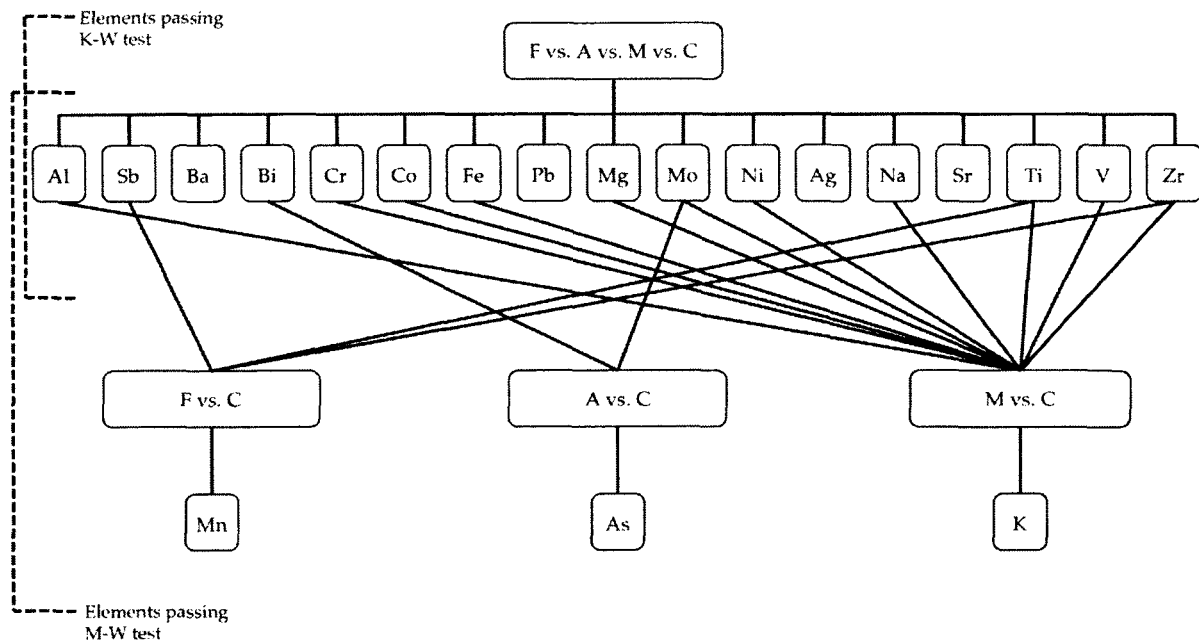


Fig. 4.6 Flow chart of elements passing the Kruskal-Wallis H -test (F vs. A vs. M vs. C) and Mann-Whitney U -tests (F vs. C, A vs. C, M vs. C). The second row shows the 17 elements that passed the K-W test. The diagonal lines connect elements in the second row with their respective M-W tests. The three elements in the bottom line passed the M-W test but did not pass the K-W test.

For forestry vs. control sites, only four of 32 properties (i.e. Sb, Mn, Ti and Zr) show significant differences (Mann-Whitney, $p < 0.05$). Therefore, the effect of for-

estry activities on suspended sediment-associated geochemical concentrations is generally not different from reference conditions.

The M-W test for agriculture vs. control land uses resulted in only three examples of statistically significant variability (i.e. As, Bi, and Mo). Therefore, as with forestry, agriculture does not differ greatly from undisturbed land use inputs to the QRB. However, it should be noted that three COI (i.e. Mn for forestry, As for agriculture, and K for mining) which passed the M-W test, are exclusive to their specific land use type. This emphasizes the importance of each respective land use to the delivery of that contaminant to the Quesnel River.

Mining is significantly different than the control sites for 12 of 32 geochemical elements. This suggests that mining activity is responsible for the greatest inter-land use spatial variability in the QRB. This, however, does not mean that the mining land use type is necessarily responsible for proportionally greater inputs of geochemical concentrations to the Quesnel River. In fact, some mean control concentrations were found to be significantly higher than those of mining. This is discussed in greater detail below.

Table 4.3 Kruskal-Wallis *H*-test values when applied to the inter-land use dataset (i.e. F vs. A vs. M vs. C)

Signature property	<i>H</i> -value	<i>P</i> -value	Signature property	<i>H</i> -value	<i>P</i> -value
Al*	11.281	0.010	Hg	5.805	0.122
Sb*	16.219	0.001	Mo*	10.370	0.016
As	7.7401	0.052	Ni*	11.890	0.008
Ba*	15.418	0.002	P	3.094	0.377
Be	3.835	0.280	K	8.069	0.045
Bi*	15.465	0.002	Se	2.912	0.405
Cd	3.352	0.340	Si	4.750	0.191
Ca	3.641	0.303	Ag*	8.397	0.039
Cr*	18.868	0.000	Na*	10.766	0.013
Co*	10.749	0.013	Sr*	9.471	0.024
Cu	2.632	0.452	Sn	6.038	0.110
Fe*	15.469	0.002	Ti*	25.398	0.000
Pb*	8.059	0.045	U	3.853	0.278
Li	7.655	0.054	V*	20.438	0.000
Mg*	12.863	0.005	Zn	3.460	0.326
Mn	7.703	0.053	Zr*	21.529	0.000

 $\chi^2_{0.05, 3} = 7.815$ * Geochemical properties with statistical significance ($p < 0.05$)

To illustrate, some of the spatial variations in geochemical properties, Figure 4.7 shows examples of box-whisker plots for select elements, for example, both Cr and Co passed the M-W test between mining and control land use types. As and Se are also displayed as elevated COI values for mining, as identified in section 3.3.2, although neither passed the M-W test.

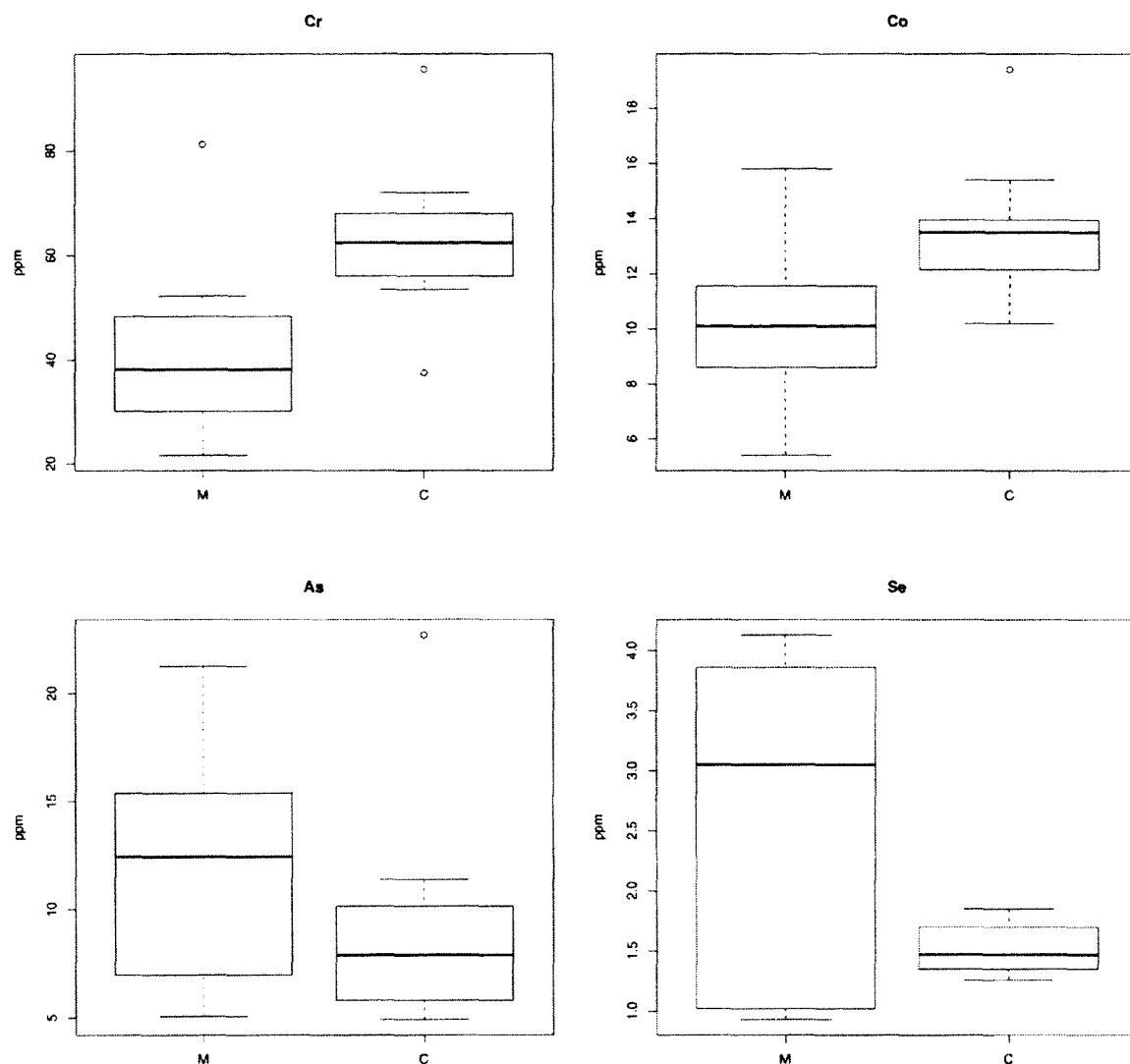


Fig. 4.7 Box-whisker plots showing the variation in values between two different land use types (mining vs. control) for a selection of elements (i.e. Cr, Co, As and Se). Cr and Co were identified as statistically different using the Mann-Whitney *U*-test, while As and Se were not but are shown here as they are of importance to suspended sediment toxicity levels based on the available literature.

For both Cr and Co, a majority of control values are higher than mining values. In fact, mean control values were higher than those for mining for 24 of 32 geochemical elements. However, mining had the highest maximum values for 20 of 32 geochemical elements. Thus, variation between a given land use (e.g. mining) and control values does not necessarily translate to comparatively greater geochemical

concentrations for that land uses. This also illustrates the advantages of using box-whisker plots in addition to the K-W test to examine differences in geochemical concentrations between the different land use categories. While the K-W test may suggest significant differences, or not, between 1 or more land use types, the box-whisker plots can help clarify patterns between groups and/or if comparisons between land use types are influenced by extreme values. This helps to narrow the search for a potential cause of variability. For example, outliers for F have a strong influence on Pb and As variability and can be further linked to a large data variation displayed by site F1 compared to sites F2 and F3 (see Figure 4.11).

Overall, mining makes the largest contribution to spatial inter-land use variation, while forestry and agriculture differ from control values only for select elements (i.e. Mn and Sb for forestry, and As and Bi for agriculture). COI concentrations do not vary significantly between all land use types but spatially elevated values (e.g. Cu and Zn for forestry; Mn for agriculture; As, Mn, and Se for mining) do exist. Sources of spatial variation can be further traced to a given sample site. To accomplish this, general descriptive statistics and rank sum tests have been applied on an intra-land use basis.

4.3.4 Spatial intra-land use variation

Variability within land use types was examined using the differences between the three replicate sample sites for each of forestry (i.e. F1, F2, F3), agriculture (i.e. A1, A2, A3), and mining (i.e. M1, M2, M3) in the QRB. Mean suspended sediment-associated concentration values for the five COIs are presented in Table 4.4. Results are separated by land use type and also include maximum and minimum values. In section 4.3.3 connections were made between elevated contaminant concentrations and specific land use types (i.e. Cu and Zn for forestry; Mn for agriculture; As, Mn, and Se for mining). In Table 4.4 land use-associated COI can be further sourced to individual sites.

Table 4.4 Mean suspended sediment-associated concentration values for contaminants of interest (As, Cu, Mn, Se, and Zn) for individual sites representing forestry (F1, F2, and F3), agriculture (A1, A2, and A3), and mining (M1, M2, and M3) land use activities. Minimum and maximum values are presented in parentheses and n = number of samples from each site.

Element	Concentration ($\mu\text{g g}^{-1}$)		
	F1	F2	F3
As	9.8 (6.2 - 13.9)	7.8 (7.0 - 9.2)	7.5 (7.0 - 8.4)
Cu	224.4 (40.0 - 611.3)	109.8 (42.4 - 349.3)	102.9 (42.1 - 178.6)
Mn	779.9 (579.1 - 1061.0)	665.4 (535.9 - 816.8)	734.8 (659.6 - 887.8)
Se	2.5 (1.4 - 5.0)	1.4 (1.1 - 1.7)	1.9 (1.4 - 2.9)
Zn	358.7 (71.8 - 1137.0)	130.8 (86.4 - 215.4)	311.0 (94.9 - 475.4)
n	4	6	4
	A1	A2	A3
As	12.0 (11.1 - 13.3)	11.5 (8.0 - 18.3)	8.3 (7.5 - 9.5)
Cu	101.8 (46.7 - 142.9)	93.5 (34.7 - 151.5)	33.4 (28.4 - 37.7)
Mn	713.9 (615.7 - 829.1)	8547.4 (717.1 - 29,009.0)	672.0 (523.4 - 1044.0)
Se	2.0 (1.7 - 2.4)	1.5 (1.1 - 2.0)	1.2 (1.1 - 1.4)
Zn	158.7 (124.1 - 235.1)	273.5 (84.7 - 1030.0)	80.1 (66.7 - 106.3)
n	5	6	5
	M1	M2	M3
As	7.5 (6.0 - 10.9)	15.0 (5.1 - 21.3)	13.9 (12.9 - 15.2)
Cu	91.1 (69.8 - 117.3)	63.7 (46.5 - 77.0)	186.6 (170.1 - 197.4)
Mn	1630.0 (1270.0 - 2319.0)	641.0 (389.0 - 1569.0)	2225.0 (1760.0 - 2786.0)
Se	3.3 (1.7 - 4.1)	1.3 (0.9 - 3.1)	3.8 (3.3 - 4.1)
Zn	129.0 (87.1 - 202.4)	60.6 (49.7 - 82.0)	251.5 (144.7 - 450.2)
N	6	6	3

Site F1 has elevated mean values for both Cu (i.e. $224.4 \mu\text{g g}^{-1}$) and Zn (i.e. $358.7 \mu\text{g g}^{-1}$), which was also responsible for maximum overall values for both COI. Site F3 was also elevated for Zn and notably had the second highest contribution of all sample sites (i.e. $475.4 \mu\text{g g}^{-1}$).

Site A2 was the single largest contributor of Mn for both mean (i.e. $8547 \mu\text{g g}^{-1}$) and maximum (i.e. $29,009 \mu\text{g g}^{-1}$) values. Again, this was likely a product of seasonal fertilizer use or livestock activity, particularly in the riparian zone.

Mean As values were elevated for both sites M2 and M3, with M2 providing the highest overall concentration (i.e. $21.25 \mu\text{g g}^{-1}$). Both sites are gold mines, for which As is a common byproduct (Azcue *et al.*, 1995). Site M2 was (and is) inactive but had not been remediated, therefore barriers to the release of residual toxins were not in place. Conversely, site M3 was an active open pit and subterranean gold mine, which was subject to modern environmental regulations for waste product storage and removal. Therefore, possible explanations for high As values were that a leak in the storage system had occurred, or toxic levels of sediment-associated As were naturally occurring in the M3 sub-basin.

Se is a potential byproduct of both copper and gold mining operations (Luoma & Rainbow, 2008), but was only elevated in the QRB for sites M1 and M3, both active mines. Although mean values were below the lethal SQG threshold, maximum values for M1 (i.e. $4.09 \mu\text{g g}^{-1}$) and M3 (i.e. $4.13 \mu\text{g g}^{-1}$) both exceeded this threshold. Again, the potential sources of Se distribution suggested for As and M3 were applicable. Lastly, Mn, also a potential byproduct of gold mining (Florea *et al.*, 2005), was elevated for site M3 and was the second highest overall source of Mn in the QRB. Maximum and mean values were several orders of magnitude lower than those collected for site A2.

All 32 geochemical elements were tested for intra-land use variation using the K-W test. For forestry (Figure 4.8) only five of 32 properties were identified as statistically significant (Kruskal-Wallis, $p < 0.05$ and $X^2 > 5.991$). This suggests considerable similarity between all three sites (F1, F2, and F3). It should be noted that of the three anthropogenically modified land uses (i.e. F, A, and M) the forestry sub-basins were in closest spatial proximity (see Figure 1.2), decreasing the likelihood of variation based on underlying geology and climate.

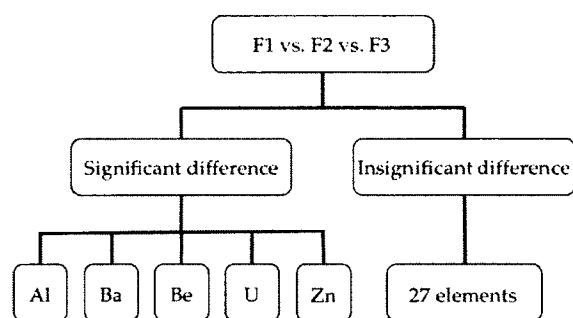


Fig. 4.8 Elements displaying significant difference between the three forestry sites (F1 vs. F2 vs. F3) as determined by Kruskal-Wallis H -test.

Inter-land use variability tests are presented for agriculture (Kruskal-Wallis, $p < 0.05$ and $X^2 = 5.991$) and mining (Kruskal-Wallis, $p < 0.05$ and $X^2 = 5.991$) in Figures 4.9 and 4.10. In both situations, a vast majority of geochemical properties passed the test suggesting that agriculture and mining had considerably more inter-land use variability than forestry in the QRB. Specifically, 29 of 32 properties passed the test for agriculture (i.e. Sb, Cd and Sn did not pass) compared to 28 of 32 for mining (i.e. Co, Ti, V and Zr did not pass).

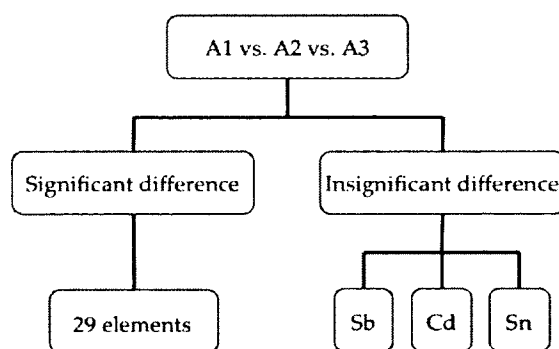


Fig. 4.9 Elements displaying significant difference between the three agricultural sites (A1 vs. A2 vs. A3) as determined by Kruskal-Wallis H -test.

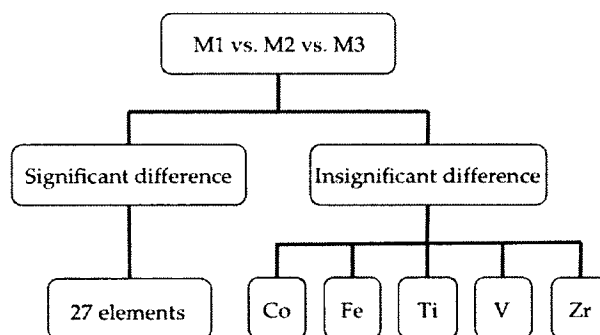


Fig. 4.10 Elements displaying significant difference between the three mining sites (M1 vs. M2 vs. M3) as determined by Kruskal-Wallis H -test (M1 vs. M2 vs. M3).

Figure 4.11 displays Cu and Zn, for forestry; of these only Zn displayed significant difference. However, both sets of box-whisker plots are visually similar. This highlights the importance of using rank sum tests to identify within land use type differences.

Conversely, box-whisker plots are useful, in addition to the statistical analysis, when identifying general trends in site-specific concentrations. These trends are important to a holistic understanding of spatial variation in the QRB, regardless of their statistical significance. In both examples site F1 provided the largest inter-quartile range and largest data spread. This supports the substantial variation associated

with site F1, which has been previously identified as a factor enhancing the influence of forestry on inter-land use variation (section 4.3.2). This trend was accentuated in several examples (e.g. As, Cd, and Se), which clearly showed greater inter-quartile ranges and predominantly elevated values for F1 compared to the other two sites. For example, Cu concentration ranges (Figure 4.11) for F1, F2, and F3 were $571.3 \mu\text{g g}^{-1}$, $306.9 \mu\text{g g}^{-1}$, and $136.5 \mu\text{g g}^{-1}$ respectively.

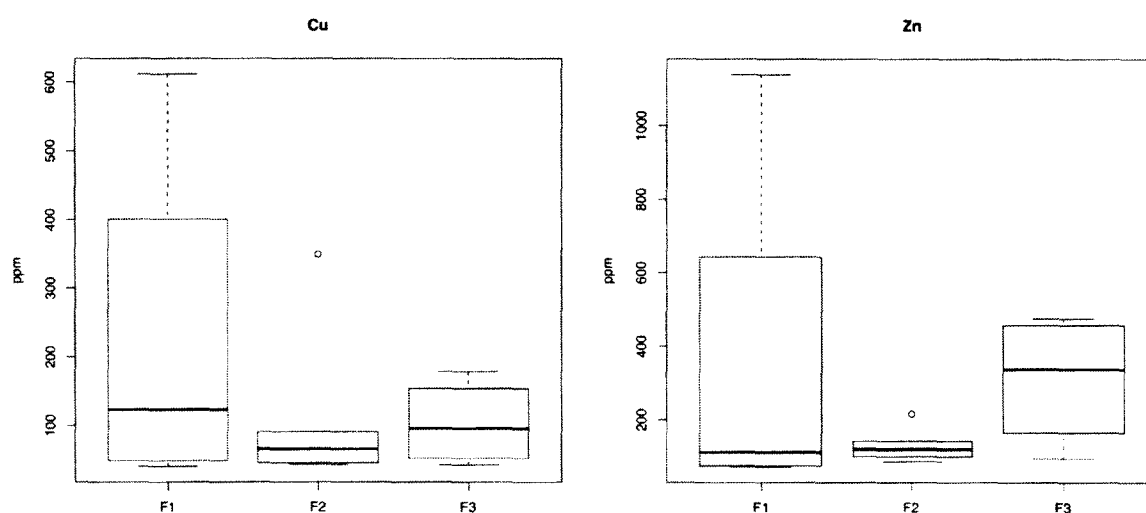


Fig. 4.11 Spatial variation in Cu (which did not pass the K-W test) and Zn (which passed the K-W test) values for the three forestry sites

Agriculture had significantly more intra-land use difference than forestry. Two COIs passing the K-W test for agriculture, which were not significant for forestry, were Mn and Se (Figure 4.12). Here, the link between Mn and site A2 is visually evident, while Se displayed a pattern of descending median concentrations between the three sites. A similar pattern, as that for Se, was found for 24 of 32 geochemical elements. The possible reasons for elevated Mn levels at A2 have previously been discussed (see section 4.32). It should be noted that all three sites did allow livestock

(cattle) entry into the stream, suggesting few barriers between field and contaminant delivery to the fluvial environment for any of the sites.

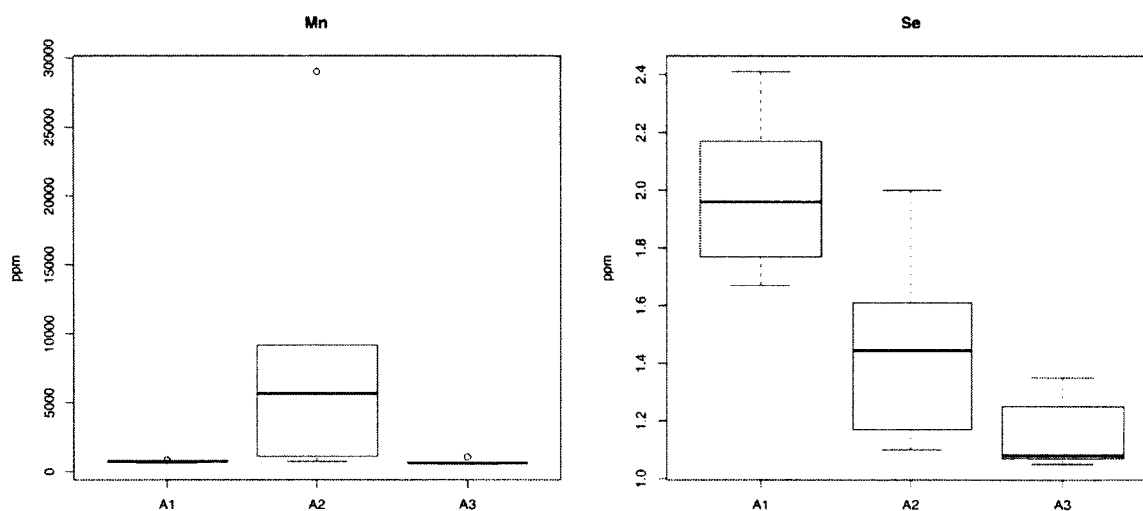


Fig. 4.12 Spatial variation in Mn and Se (which passed the K-W test) values for the three agricultural sites

For mining sites, four of the COIs (i.e. As, Cu, Mn, and Se, Chapter 3) that displayed significant intra-site difference are presented in Figure 4.13. As a reminder, sites M1, M2, and M3 represent an active open-pit copper mine, an inactive hydraulic gold mine, and an active open-pit and subterranean gold mine, respectively. As a notable difference, M2 showed comparably low concentration values for Cu, Mn, and Se, although single elevated values close to M1 and M3 means were recorded in J-A for this site (see section 4.3.2) and appear as outliers in Figure 4.13. In contrast, site M2 was elevated for As, while sites M1 and M3 had considerably lower values. These examples suggested that intra-land use variation for mining may have been linked to differences between inactive (but not remediated) and active mine sites.

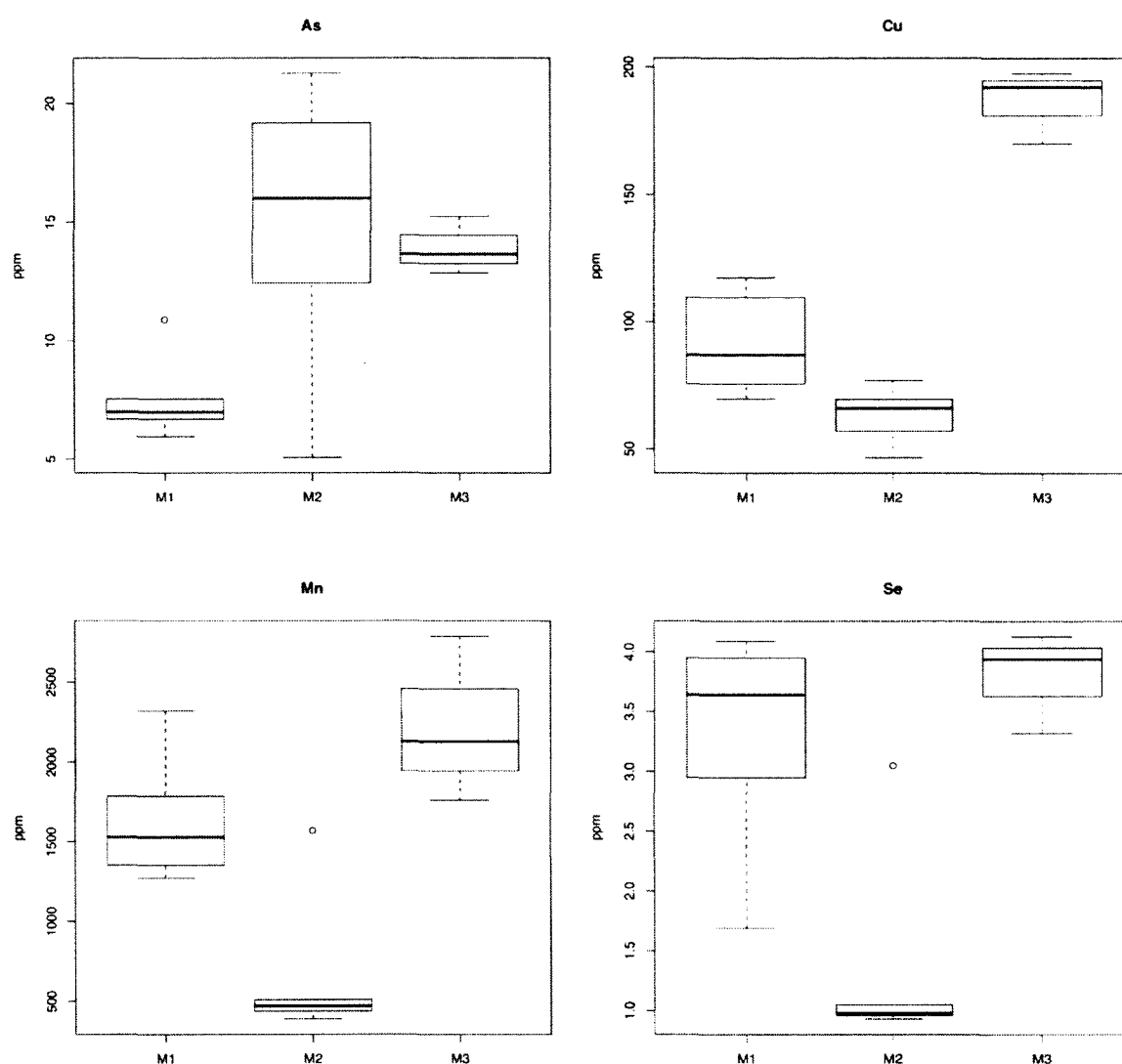


Fig. 4.13 Spatial variation in As, Cu, Mn and Se (which passed the K-W test) values for the three mining sites

Results for spatial intra-land use variability suggested agriculture and mining sites exhibited more significant difference than forestry sites. For forestry, site F1 was often elevated above values for F2 and F3. Site A2 was substantially elevated for Mn, but for a majority of geochemical elements exhibiting statistically significant difference, there was a decrease in mean concentration from site A1 to A3. Most mining-associated intra-land use variation seemed to stem from differences in output

between active (i.e. M1 and M3) and inactive (i.e. M2) mine sites. In general, active mine-associated geochemical concentrations were elevated. One main exception was As, which was high for M2, and was likely either occurring in high concentrations naturally or reflected a legacy effect of specific mining activities.

4.4 Conclusions

Fine-grained suspended sediment was collected from streams draining different land use activities in the QRB. While mean metals and nutrient values for the control sites exhibited little variation over the sampling period (April–October 2008), there were more pronounced temporal variations for streams draining catchments impacted by forestry, agricultural and mining activities. Generally, metal and nutrient concentrations for impacted sites were greater than for control sites.

Analysis of temporal inter-land use variation determined that the overall mining signature behaved as a point source and was often a function of changes in source inputs and delivery. Conversely, forestry and agriculture behaved as diffuse sources and were influenced by variations in transport conditions (e.g. PPT and Q). Thus most fluctuations in mining values were independent of PPT and Q patterns. Conversely, forestry and agriculture exhibited highest concentrations during higher flow conditions and PPT levels.

Consistent trends in temporal intra-land use variation included links between PPT and sites F1, A2, and M2, particularly during J-J and J-A. Of the mining sites, M1 appeared to fluctuate independently of either PPT or Q temporal patterns, suggesting mine activity, rather than natural geochemical introduction, plays the more important role. For sites F1, A2, and M3, substantially elevated contaminant levels were attributed to the interplay of seasonal thaw conditions and increasing PPT dur-

ing J-J. Finally, a spike in Mn noted during inter-land use analysis for agriculture was sourced to site A2. This value occurred during peak PPT values, but the absence of a spike for sites A1 or A3 suggests that greater livestock activity or fertilizer use, particularly in the riparian zone, also influenced the A2 data.

Spatial inter-land use variation was predominantly due to differences in geochemical concentrations between mining and control sites. Forestry and agriculture differ from control sites for select elements, but play a lesser role than mining. In general, COI concentrations were not significantly different between all land use types.

Agriculture and mining sites exhibited significantly more intra-land use spatial difference than forestry sites. Site F1 in particular is disproportionately elevated for forestry, as is site A2 for Mn. Mining-associated variation was attributed to differences between active and inactive (i.e. M2) mine sites, where active sites generally produced elevated geochemical concentrations.

CHAPTER 5: BASIN SCALE EXTRAPOLATION

5.1 Introduction

Provenance-based fingerprinting and signature determination has advanced significantly over the past three decades and has involved several techniques during this time. These methods include the use of profilometers (e.g. Toy, 1983), soil erosion plots (e.g. Loughran, 1989), and field observations and mapping (e.g. Lao & Coote, 1993). More recent practices have employed the use of erosion pins (e.g. Lawler *et al.*, 1997), terrestrial photogrammetry (e.g. Collins & Moon, 1979; Barker *et al.*, 1997), and remote sensing (e.g. Bryant & Gilvear, 1999; Vrieling, 2006). The contemporary fingerprinting technique used in this study (Collins *et al.*, 1996; Collins & Walling, 2004; Walling, 2005) is another approach that is being increasingly used to identify sources of sediment and associated contaminants and which is both cost effective and reliable (Davis & Fox, 2009; Larsen *et al.*, 2010).

This chapter addresses research objective 3 (Chapter 1). In Chapter 4 (see section 4.3.1.1) potential signature properties were derived from a list of 32 geochemical elements using the Kruskal-Wallis *H*-test (K-W test). This chapter refines the signature using stepwise discriminant function analysis (DFA), resulting in a composite signature capable of differentiating correctly 100% of the source geochemical contributions from each of forestry, agriculture, mining, and control land uses. A multivariate mixing model then utilizes the geochemical concentrations for each of the composite signature elements, recorded at site Q2, to determine the relative contribution from each land use type. Since site Q2 is at the river outlet, and the approach apportions where in the upstream basin the sediment at site Q2 has originated, this is called a *bottom-up* approach.

5.2 Methods

5.2.1 Sampling and laboratory analysis

The field and laboratory methods used, from sample collection to determination of elemental concentrations, have been described in detail in Chapter 3 (see section 3.2). Briefly, land use-associated samples were collected between April and October 2008. Suspended sediment was collected using the time-integrated Phillips sampler (Phillips *et al.*, 2000) at monthly intervals from 13 sites representing forestry (F), agriculture (A), mining (M), and control (C) land uses.

In the laboratory, a range of base cations, heavy and trace metals, and nutrients, totaling 32 geochemical properties, were selected for analysis. Sediment samples were sieved to $<63\ \mu\text{m}$, freeze-dried, and processed using acid and microwave digestion using nitric and hydrochloric acids. Chemical concentrations were then determined using inductively coupled plasma mass spectrometry (ICP-MS) at UNBC.

5.2.2 Land use discrimination

The process of distinguishing between source materials (land uses) through composite signature creation required two stages. That is, a two-stage statistical selection procedure, originally presented in Collins *et al.* (1996), was used to decrease the initial list of potential signature properties (32) to a more manageable number (i.e. 6 in this study). The refined signature was then capable of discriminating explicitly among the land use-associated sub-basins of the QRB.

Stage one has previously been explored in detail in Chapter 4 (see section 4.3.1.1). In this stage, all potential signature properties were tested using the non-parametric K-W test (Kruskal & Wallis, 1952) for its ability to identify statistically significant

variability (i.e. F vs. A vs. M vs. C). All individual properties failing the tests were removed from future consideration. Geochemical elements passing the test and proceeding to stage two included: Al, Sb, Ba, Bi, Cr, Co, Fe, Pb, Mg, Mo, Ni, Ag, Na, Sr, Ti, V, and Zr. Thus the number of candidate signature properties typifying inter-land use variability was reduced from 32 to 17.

Stepwise DFA was used in the second stage to identify a composite signature capable of differentiating correctly 100% of the source geochemical contributions representative of each land use. The analysis used a stepwise selection algorithm based on the minimization of Wilk's lambda.

In general, DFA is used to determine whether two or more groups differ with regard to the mean of a variable, and that variable is subsequently used to predict group membership. With multiple variables, stepwise DFA can be performed. At each step of analysis, all variables are reviewed and evaluated. In forward stepwise analysis, as used in this study, the variable that contributes the most to the discrimination among groups is included in the signature. Once a variable has been selected, the process restarts (a new step) and the variable with the next most prominent contribution to discrimination is determined and added to the signature. Additional steps are then conducted until all groups can be correctly classified through the cumulative differentiating ability of the selected variables.

Conversely, in backward stepwise analysis, the variable contributing the least to group classification is removed at each step, until the most important and influential variables remain.

All statistical analyses used in creating a QRB-representative composite signature were conducted using R 2.12.1 (2010) with the MASS (Venables & Ripley, 2002) and

klaR (Weihs *et al.*, 2005) packages. Stepwise DFA was conducted with R programming guidance, through the R-help network, from Bill Venables of the Commonwealth Scientific and Industrial Research Organization (CSIRO); Australia's national science agency. Full-form R scripts are presented in Appendix A4.

The final results of the composite signature selection procedure are presented in Table 5.1. Although 100% of the land use samples were classified correctly after four steps, an additional two steps were conducted, resulting in a composite signature with six properties. The extra information provided by adding a select number of signature variables after the 100% discrimination threshold has been surpassed, such as Co and Mo in this case, has been found to enhance the discriminating reliability of the composite signature (Walling *et al.*, 1993; Collins *et al.* 1997c), while still keeping the number of properties used in the unmixing model to a manageable number (i.e. 6).

Table 5.1 Stepwise discriminant function analysis results for the QRB.

Signature property	Cumulative % land use samples classified correctly
V	58.3
Mg	83.3
Al	95.8
Zr	100
Co	100
Mo	100

It should be noted that the geochemical elements emerging from the stepwise DFA may include spatial geological inputs in addition to land use inputs. However, land use-associated geochemical element concentrations are generally higher than background concentrations in the QRB (see Table 3.3), supporting the use of stepwise DFA results in the QRB composite signature.

5.2.3 Multivariate unmixing model approach

Under the presumption that the composite signature property concentrations collected from the predominant land uses in a basin (i.e. F, A, M and C) can be used to predict the concentrations expressed in the basin outlet signature (i.e. at Q2), a multivariate unmixing model (Collins *et al.*, 1996) was applied to the QRB. The unmixing model has been used in several studies for sediment source ascription (e.g. Collins *et al.*, 1997a, 1997b, 1997c; Russell *et al.*, 2001; Walling *et al.*, 2008) and is based on the optimization of the sum of squares of the deviations between measured and estimated concentrations for a given suspended sediment sample. Collins *et al.* (2010) represents one of the most recent and comprehensive application of the model to date. In this present study, fewer weighting factors are included than in Collins *et al.* (2010), due to both comparatively limited data and arguments countering the inclusion of some factors (e.g. not including an organic matter correction factor; described below).

The mixing model is bound by two constraints: (1) the relative contributions (P_s) from the individual land use-representative sediment sources are non-negative (Eq.(5.1)) and (5.2) the summed contributions must equal unity (i.e. 100%) (Eq.(5.2)).

$$0 \leq P_s \quad (5.1)$$

$$\sum_{s=1}^n P_s = 1 \quad (5.2)$$

The comprehensive Collins *et al.* (2010) mixing model algorithm minimizes the sum of squares of the weighted relative errors to estimate the relative contributions from sediment sources, as in the original Collins *et al.* (1996) example. However, additional property weightings are included in the contemporary version of Collins *et al.* (2010) (Eq.(5.3)):

$$\sum_{i=1}^n \{ (C_i - (\sum_{s=1}^m P_s S_{si} Z_s O_s SV_{si})) / C_i \}^2 W_i \quad (5.3)$$

where n=number of signature properties comprising the optimum composite signature; C_i =concentration of signature property (i) in the land use-associated sediment collected from the sub-basin outlet; m=number of land use-associated sediment source categories. P_s = the optimized percentage contribution from land use category (s); S_{si} =mean concentration of signature property (i) in land use category (s); Z_s =particle size correction factor for land use category (s); O_s =organic matter content correction factor for land use category (s); SV_{si} =weighting representing the within-land use variability of signature property (i) in land use category (s); W_i =signature property discriminatory weighting.

In the QRB study, the mixing model algorithm is similar to earlier permutations, as several property weightings, although validated within the scope of Collins *et al.* (2010), were removed from the equation (Eq.(5.4)) viz:

$$\sum_{i=1}^n \{ (C_i - (\sum_{s=1}^m P_s S_{si} Z_s)) / C_i \}^2 \quad (5.4)$$

In Eq. (4) property weightings O_s , SV_{si} and W_i were discarded while P_s , S_{si} and Z_s were retained from Eq. (5.3). Thus in the case of the organic matter correction factor (O_s), although carbon and nitrogen data were measured in the QRB sediment samples, O_s correction was not used in the QRB mixing model. As a component of suspended sediment, organic matter has been documented as a scavenger of chemical elements from the water column, such as the trace metals in the composite signature, thereby enhancing the trace metal retention ability of the sediment (Peart & Walling, 1986; Horowitz, 1991). However, Walling *et al.* (1999) suggests that the trace metal content and organic matter content relationship is complex and generalizations about this relationship are prone to inaccuracy. Thus, attempts to quantify this relationship are subject to the same sources of complexity and inaccuracy. Considering that an organic matter correction may actually be a source of error in the QRB mixing model and subsequently result in signature property over-correction (Carter *et al.*, 2003), it was omitted from the model.

Precision associated with the laboratory measurement of each geochemical has previously been addressed using replicate measurements and expressed in the mixing model as a signature property-specific weighting factor (W_i) (e.g. Collins *et al.*, 1996). It was not possible to create a reliable (W_i) correction factor in the QRB study as most sediment samples were too small (i.e. < 0.5 g) to allow replicate laboratory testing. Therefore, the W_i weighting factor was not used in this study.

In Collins *et al.* (2010) – with reference to Small *et al.* (2002, 2004) – a weighting representing within-land use variability (SV_{si}) was added to the mixing model equation (Eq. 3) to ensure that the land use with the smallest standard deviation contributed the most to the model solution. In the QRB study, the small number of sample

sites contributed to a situation in which one site (i.e. F2) was left representing the entire geochemical signature for a given land use when certain sites (i.e. F1, F3 and M3) dried-up during the sample season. With only one signature source, there is no variation, which, according to the SV_{si} weighting factor, would give that site a representation advantage over other land uses with greater within-land use variation. This scenario seems unrepresentative of conditions in the QRB, particularly when variability results for previous months are considered. For example, during M-J, J-J and J-A, forestry displayed the highest within-land use variability for Al (one of the geochemical elements selected through stepwise DFA for the basin-scale signature). However, only one stream was active for forestry during A-S and S-O, resulting in zero intra-site variability and a dramatic change in land use variability rankings. With reference to the small sample population and extrapolated temporal intra-site variability patterns of the QRB, the SV_{si} weighting factor was expected to increase error in the mixing model and, therefore, was removed from the equation.

Differences in grain size have been linked to variation in sediment-associated geochemical concentrations (Horowitz, 1991). Although sieving of sediment to $<63 \mu\text{m}$ was a good initial step, in order to enable direct comparison between sediment samples, it was necessary to introduce a particle size correction factor (Z_s). In this study, the correction factor was based on a well-established procedure (He & Walling, 1996; Walling *et al.*, 1999; Russell *et al.*, 2001) using the ratio of the mean specific surface area of the basin outlet (Q2) samples to the corresponding means of land use-associated samples (see section 4.2.2 for expanded methods). In this manner, two groups of land use-associated Z_s values were established representing early (May-July) and late (August-October) periods of the sampling campaign. All land

use category grain sizes were corrected to enable comparison to the downstream Q2 sample, the intended location of basin-scale composite signature-based extrapolation. This correction ensures that the mixing model solutions are less susceptible to particle size-related errors. It should be noted that analysis could not be conducted for the A-M sample period as the Q2 sampler was lost during high flood discharges.

Multivariate mixing model analysis was completed using the *Solver* add-in with *Microsoft Excel for Mac version 12.2.9*. The model was given a maximum run time of 600 seconds in which to conduct 5000 iterations at a precision of 0.000001 and tolerance at 5%.

5.3 Results and discussion

5.3.1 Multivariate mixing model-based extrapolation

The multivariate mixing model was used to determine the relative contribution of each land use category to monthly suspended sediment-associated signatures representing the basin outlet site on the Quesnel River (i.e. site Q2). Figure 5.1 presents the resulting contributions from each land use type for each sample period.

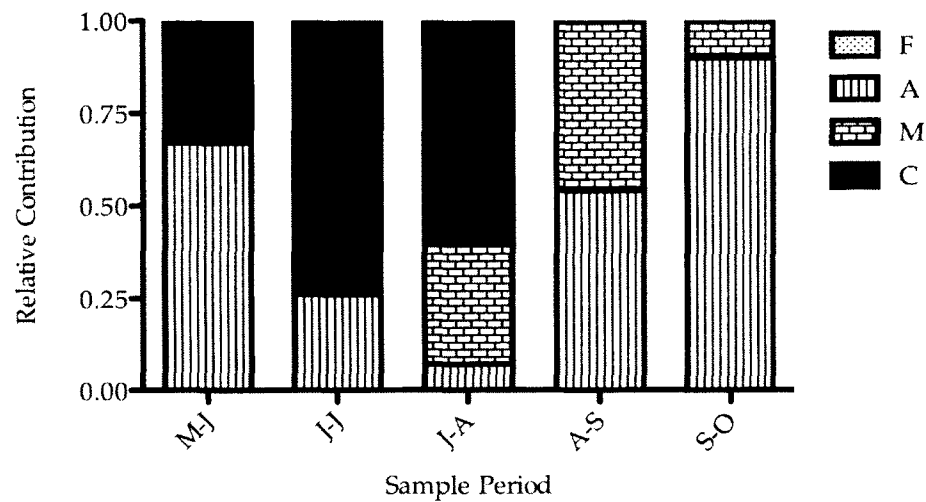


Figure 5.1 Relative contributions to the QRB outlet (site Q2) from different land use types (i.e. F=forestry, A=agriculture, M=mining, and C=control), estimated using a multivariate mixing model-based approach. Sample periods are represented from May to October, 2008 (May-June (M-J), June-July (J-J), July-August (J-A), August-September (A-S), September-October (S-O)).

The unmixing model solution attributes agriculture with the largest (average over full sampling period = 49%) overall contribution to the geochemical signature at the QRB outlet. This contribution is strongest in the S-O (90%), M-J (67%), and A-S (54%) sample periods, declining to 7% in the mid-summer (J-A) sample period. The control/reference land use signature provides the second largest contribution over the full sampling period (e.g. average = 33%) and is restricted to the first three sample periods. Mining (e.g. average = 18%) contributes most to the QRB outlet signature in the final three sampling periods (i.e. J-A, A-S and S-O). Forestry land use (average = 0%) does not appear to contribute to the sediment collected at Q2, or its contribution is so low (say <5%) that it is not recognized by the unmixing model. Other authors (e.g. Walling et al., 1999) have also stated that a value of 0% for a particular source type does not necessarily mean that that source contributed no sediment.

The strong relative contribution from agriculture is in keeping with the high ero-

sion rates associated with agricultural land use, both arable and pasture (Morgan, 2005), and the high sediment delivery ratio due to limited riparian buffers. It may also be due to the close proximity of most agricultural land uses to the Q2 site, as agriculture is prominent in the lower, flatter reaches of the QRB. The dipping of the agriculture contribution during mid-summer may be due to a lack of rainfall events during this time. That is, deforested and livestock-disturbed fields are susceptible to overland sediment transport predominantly during intense rainfall events, compared to point sources (e.g. mine sites). This corresponds with findings from Chapter 4 (see section 4.4), where temporal inter and intra-land use variation was linked to changes in precipitation (PPT). Specifically, highest concentrations from diffuse sources (i.e. forestry, agriculture, and control) were exhibited during higher discharge conditions and peak PPT levels. Conversely, mining functioned independently of discharge or PPT trends. Thus, the higher mining output recorded in A-S (46%) correspond to the period of lowest seasonal discharge and PPT (Figure 5.5) and may reflect mining operations at this time.

The lack of representation of forestry in the Q2 signature is somewhat surprising given the often high erosion rates often cited for this land use (Morgan, 2005). However, the finding is consistent with the current management plans for forestry operations whereby it is common to install riparian buffer zones to prevent sediment and associated contaminants from reaching river channels. It is also consistent with other research in the QRB (e.g. Caley, 2011), which has demonstrated that riparian zones and wetlands may play an important role in trapping sediment from forestry operation and reducing downstream fluxes to watercourses.

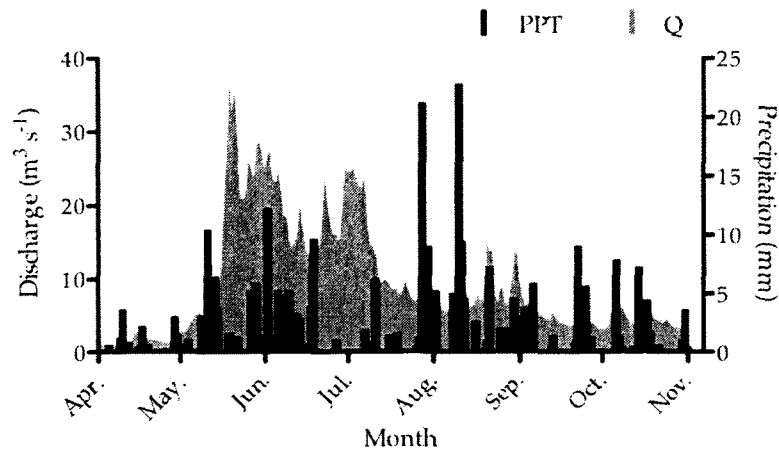


Figure 5.2 Total daily precipitation (PPT) and discharge (Q) values representing site Q2. Values were recorded during the 2008 field season at the Quesnel Airport meteorological station (Environment Canada, 2011) and a Water Survey of Canada gauging station near Quesnel (WSC, 2010).

The QRB meteorological data (Environment Canada, 2011) presented in Figure 5.2 shows high precipitation during spring (M-J) and late summer (A-S) of 2008. There may be a relation between a low relative agricultural contribution and the lowest precipitation values found between late June and late August, and for some temporal delay of sediment transport from land use-associated sub-basins to the basin outlet. Also of note in Fig. 5.1 is the relatively high contribution from the control/reference land use. This may reflect the fact that this land use is dominant in the study area. The importance of control/reference land use during the first half of the sampling period may reflect the importance of prolonged and extensive snow melt over large parts of the watershed in supplying sediment to channels, relative to rainfall events in the later months which are typically less erosive in highly vegetated areas.

It is also important to recognize that land use-associated suspended sediment fluxes are subject to temporal delays between mobilization and transport at down-

stream locations, such as Q2, due to hydrologic travel distance and barriers to delivery into and through the stream network, and temporary storage effects (on the channel bed, in bars etc). Thus, the relative land use proportions of the QRB signature determined for site Q2 likely represent sediment and geochemical element delivery during both recent and previous time periods. For example, the higher relative mining outputs for J-A and A-S were probably introduced to the main channel in J-J or earlier (Phillips & Southerland, 1989; Dadson & Church, 2005). This study has not determined such time-lag effects between sources and sinks, however it is important to recognize such effects and future studies should address this. Furthermore, this study has not considered the impact of channel bank erosion as a source of the sediment and contaminants collected at Q2. It is important to note that bank sediment samples were not collected and characterized as part of this fingerprinting exercise. This may be important in that the literature suggests there are differences between sediment from banks and other fluvial sources (Taylor *et al.*, 2008). In particular, bank sediment has been associated with introducing background “clean” sediment to the fluvial environment and sometimes diluting the more concentrated geochemical signature from bed or suspended sediment sources.

5.4 Conclusions

A sediment fingerprinting approach was used to predict the suspended sediment-associated geochemical signature at the QRB outlet and determine the relative input from different land uses active in the basin. The multivariate unmixing model determined that agriculture was the highest overall contributor, while the control/reference land use influence was strongest earlier in the sampling campaign

(i.e. M-J, J-J and J-A) and mining contributed most in the latter sampling periods (i.e. J-A, A-S and S-O) possibly reflecting mining operations during this time. The prevalence of the agricultural input may be due to the close proximity of agriculture-dominated sub-basins to the downstream site Q2 at Quesnel, relative to other land uses. Additionally, agricultural sites are commonly associated with high soil erosion rates and sediment delivery ratios. In addition, they had limited to no riparian buffer zone between actively disturbed fields and study creeks, suggesting limited barriers to sediment delivery into the river system. The importance of the control/reference land use is likely to reflect the areal dominance of this land use, while the negligible contribution from forested land use may be due to the role of riparian buffers installed as part of harvesting management plans in watersheds.

CHAPTER 6: CONCLUSIONS

“Water is fundamental for life and health. The human right to water is indispensable for leading a healthy life in human dignity. It is a pre-requisite to the realization of all other human rights.”

-- The United Nations Committee on Economic, Cultural and Social Rights

6.1 Main findings and implications of results

This thesis demonstrates the importance of fine suspended sediment as a vector of geochemical transport from different land uses in the QRB. Fine-grained suspended sediment was collected from streams draining different land use activities in the QRB. Concentrations of geochemical elements (in particular nutrients and metals) were then compared to national and international SQGs. Temporal and spatial patterns of geochemical values for sediment were also compared and contrasted between and within land use types. Finally, a multivariate mixing model was used to predict the relative contributions of each land use to the basin outlet at Quesnel. In order to assess the representativeness of the raw sediment data, a flume-based evaluation of the Phillips time-integrated suspended sediment sampler was also conducted.

Chapter 3 presents the contaminant concentrations of fine suspended sediments associated with different land use activities (i.e. Objective 1). Generally, metal and nutrient concentrations were greater for impacted sites compared to control sites. Geochemical element concentrations approached or exceeded SQG upper thresholds in several instances, which may be detrimental to river health. Namely, concentrations of As, Cu and Mn for mining sites, Cu and Zn for forestry sites, and Mn for agriculture sites, have all reached levels of potential toxicity and are contaminants of interest (COI). Additionally, mining sites were associated with elevated levels of Se, which is also included as a COI. For suspended sediment in the QRB, metal mining,

and to some extent forest harvesting, exerted greater influence on the concentration of sediment-associated metals and nutrients than agricultural activities.

For bed sediment, As and Se exceeded upper SQG thresholds for mining sites, while Mn and Se exceeded the same thresholds for agricultural sites. A larger number of lower SQG thresholds are surpassed by geochemical element concentrations associated with bed sediment than with suspended sediment.

Overall QRB health, as determined by fine sediment quality through SQGs, is complex and difficult to define at the basin scale due to significant spatial variations. However, pockets of contamination do exist for several geochemical elements, which are linked to certain land use activities.

Spatial and temporal differences between and within land use types were examined in Chapter 4 (i.e. Objective 2). Here, control sites exhibited little variation for mean geochemical element concentrations over time, while larger temporal variations were common with impacted land use types (i.e. forestry, agriculture and mining).

Analysis of temporal variation between land use types reveals that the mining signature was related to point source inputs and delivery associated with mining operations, while forestry and agriculture were dependent on precipitation (PPT) and discharge (Q) changes over time, which is indicative of diffuse source inputs.

Examination of intra-land use variation reveals temporal links between precipitation (PPT) and sites F1, A2 and M2. This is most prominent during June-July and July-August sampling periods. Conversely, mining site M1 fluctuates independently of PPT and Q temporal patterns. This suggests that point source mining activities, rather than natural geochemical transport processes, are responsible for geochemical

inputs, in this case. Additionally, in June-July, sites F1, A2 and M3 have elevated contaminant levels due to increasing PPT and seasonal thaw conditions. That is, delivery of sediment during early sampling periods is likely inhibited by frozen soil conditions in some areas. Finally, site A2 is responsible for a spike in Mn concentration during July-August, which is also associated with peak PPT values. The lack of a Mn spike for sites A1 and A3, during the same sampling period, suggests that comparatively greater fertilizer use or livestock activity in the riparian zone is occurring at site A2.

Geochemical element concentrations for mining and control/reference land uses are responsible for the greatest spatial inter-land use variation in the QRB, while agriculture and forestry, although statistically different for some geochemical elements, do not stand out.

In terms of spatial intra-land use variability, agriculture and mining sites vary more significantly than forestry. However, site F1, for several geochemical elements, appears elevated compared to sites F2 and F3, although these differences are not statistically significant. Again, site A2 is linked to elevated Mn levels and this spatial difference is confirmed to be significant by rank sum tests. Additionally, active mining sites are generally associated with elevated geochemical element concentrations compared to inactive sites (i.e. M2), accounting for some intra-land use variation.

For bed sediment, concentration values are similar or lower than for suspended sediment. However, elevated levels of Se for bed sediment- for all land use types are a notable exception.

In Chapter 5 a suspended sediment-associated geochemical signature was predicted for the QRB outlet using an established and widely used sediment finger-

printing approach which uses a multivariate unmixing model (i.e. Objective 3). The results demonstrated the relative input from different land use types to suspended sediment geochemistry at Quesnel (i.e. site Q2). Specifically, agriculture is the highest contributor overall (average = 49%). An elevated influence of control/reference land use is present between M-J and J-A. Likewise, the mining influence is noticeable between J-A and S-O. The relative prominence of the agricultural input is likely due to the close proximity of agriculture-dominated tributaries to site Q2, and the minimal riparian zone observed at some agriculture sites, promoting sediment transport.

Lastly, it was necessary to test the effectiveness of the primary field sampling equipment for this study (i.e. Objective 4); the Phillips time-integrated suspended sediment sampler. In Chapter 2, the sediment mass and grain size efficiency of the sampler was evaluated in flume-based trials using kaolinite and natural Quesnel river sediment. The Phillips sampler displayed preferential selection for coarser sediment for the kaolinite trials but not for the river sediment. Efficiency results are similar to those presented in Phillips *et al.* (2000). Possible sources of inefficiency include through-flow of very fine-grained sediment and settling of the coarsest grains on the flume bottom. There was also little difference in grain size between sediment captured by the Phillips sampler and adjacent channel bed sediment. When compared (Phillips sampler sediment – channel bed sediment) some coarsening was found in mining channels (+4.4 μm), while notable fining was associated with the Quesnel River main channel (-6.3 μm). Overall, the Phillips sampler collects a time-integrated sample of suspended sediment which is representative (in terms of composition) of ambient conditions. However, some anchorage modifications suggested

in McDonald *et al.* (2010), which keep the sampler's nose cone pointed into the current and automatically varies with changes in depth, may improve sediment collection.

6.2 Limitations of the research

In retrospect, a few factors lead to difficulties during, and limitations of, this project. First, a limited number of samples were collected. That is, a maximum of only three samples for each land use type were collected each month. That left the study vulnerable to gaps in the dataset, and indeed some samples were not collected at certain times due to drought conditions or actual loss of the sampler. Fewer samples also limited the statistical tests that could be conducted to produce statistically significant results.

Similarly, sampling was only conducted over six months in 2008. This did not allow for replicate sampling from year to year and limited the scope of the project to the snow-free period of 2008. If there was an additional field season, annual changes in PPT and Q regime could be incorporated into the analysis.

A more complete study would also include bed sediment samples for all months instead of just the final three sampling periods. Quesnel River bank sediment was also not sampled, ignoring a source of natural sediment input, which influenced the results of the unmixing model. Sampling from the above-mentioned locations could have enabled a more holistic understanding of sediment-associated geochemical distribution in the QRB.

6.3 Recommendations for future research

In future studies of suspended sediment in the QRB, it would be useful to sample from a greater number of sites and over additional field seasons. This would result in greater replicate sampling and more robust statistical analysis. Further, to safeguard against gaps in the dataset, two or more Phillips samplers could be placed at each sampling location in case of sampler loss during flood conditions or due to vandalism.

Topsoil and subsoil samples from each land use type would also help to clarify sediment source locations prior to the mixing of natural bank sediment and anthropogenic inputs in the fluvial environment. As such, bank sediment could also be sampled from tributaries and the main Quesnel River channel to separate the influence of channel bank inputs on suspended sediment-associated geochemical concentrations. Further sampling of bed sediment would also strengthen an understanding of geochemical distribution in the river channel by providing information on potential storage sites (and thus time-lags of sediment transport) and potential geochemical transformations at such sites.

Modifications to the Phillips sampler anchorage system suggested in McDonald *et al.* (2010) should be implemented. These changes leave the sampler responsive to changes in current direction and keep the sampler's nose cone pointed into the current, much like a weathervane with the wind. The system also automatically varies sampler depth with changes in river water depth. Both modifications should increase the collection of sediment in the sampler.

An additional area for further research would be to analyse sediment samples for additional properties that are diagnostic of different land use activities. In this study,

attention was focused on geochemical elements (in particular trace metals and P). Further work could focus on sediment-associated properties such as pathogens and organic properties (persistent organic pollutants), which are often specific to a certain land use activity (e.g. agriculture). Such properties, in combination with trace metals and nutrients, may provide a more robust way of distinguishing land use activities on sediment properties.

6.4 Concluding thoughts

Focused and continuous monitoring of the most toxic sites in the QRB, once identified by preliminary results, could be an effective way to allocate resources and time to determine the greatest threats to river health. Such focused sampling would also limit the chance of missing high concentration contaminant fluxes (e.g. due to storm events or settling pond failures). Furthermore, detailed recording of known polluters (e.g. as identified by comparison to SQGs) could be useful as evidence in legal action, with the goal of cessation of contaminant inputs and remediation of any polluted areas by those responsible. Ultimately, more robust sampling and analysis would strengthen the ability of this project, and ones like it, to positively affect river health and in particular stewardship of the QRB.

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APPENDIX A1: Evaluation of the Phillips sampler: calculations and results

Calculations and variables used in sampler evaluation:

- Inlet tube cross-sectional area = $\pi r^2 = \pi(0.2 \text{ cm})^2 = \pi(0.04 \text{ cm}^2) = 0.126 \text{ cm}^2$
- Trial duration = $60 \text{ s/min} \times 60 \text{ min/h} \times 6 \text{ h} = 21600 \text{ s}$
- Sampler volume (measured) = 8.68 L
- Ambient suspended sediment concentration (SSC) = $200 \text{ g}/(1232 \text{ L flume} + 10 \text{ L sample bucket}) = 0.161 \text{ g L}^{-1}$
- Inlet tube flow velocity = 6.6 cm s^{-1}

= Non-isokinetic nature of sampler calculation (Eq. (1)) as determined experimentally in Phillips *et al.* (2000).

$$y = -2.182 + 2.074(x) \quad \text{Eq. (1).}$$

where y is the logarithmic water flow velocity in the Phillips sampler inlet tube, and x is the logarithmic water flow velocity in the flume

$$x = \log(28 \text{ cm s}^{-1}) = 1.45$$

$$y = -2.182 + 2.074(1.45)$$

$$y = 0.82$$

$$\text{Therefore: Inlet tube flow velocity} = 10^{0.82} = 6.6 \text{ cm s}^{-1}$$

Volume of water passing through sampler during trial:

=The product of the inlet tube cross-sectional area, the inlet tube flow velocity, and the trial duration, plus the volume of the sampler, to account for initial SSC.

$$= 0.126 \text{ cm}^2 \times 6.6 \text{ cm s}^{-1} \times 21600 \text{ s} + 8.68 \text{ L}$$

$$= 17962.56 \text{ cm}^3 + 8.68 \text{ L}$$

$$= 17.96 \text{ L} + 8.68 \text{ L}$$

$$= 26.64 \text{ L}$$

Discharge at sampler inlet:

= Product of the inlet tube cross-sectional area and the inlet tube flow velocity

$$= 0.126 \text{ cm}^2 \times 6.6 \text{ cm s}^{-1}$$

$$= 0.832 \text{ cm}^3 \text{ s}^{-1} \text{ (since 1 cubic cm} = 1 \times 10^{-6} \text{ cubic m)}$$

$$= 8.32 \times 10^{-7} \text{ m}^3 \text{ s}^{-1} \text{ or } 8.32 \times 10^{-4} \text{ L s}^{-1}$$

Rate at which the volume of water in the sampler is replaced:

= Trial duration / sampler refresh time

$$8.32 \times 10^{-4} \text{ L / s} = 8.68 \text{ L / X s}$$

$$\text{X s} = 8.68 \text{ L} / 8.32 \times 10^{-4} \text{ L}$$

$$\text{Xs} = 10437.7 \text{ s}$$

Therefore:

Every 10437.7 s, 8.68 L of “clean” water enters the flume and SSC (in g L^{-1}) \times 8.68 L is removed from the ambient flume SSC.

Reduction in SSC due to sampler retention of suspended sediment:

Number of iterations during trial = Total trial duration / sampler refresh time

$$= 21600 \text{ s} / 10437.7 \text{ s}$$

$$= 2.07 \text{ iterations}$$

EFFICIENCY OF SAMPLER USING TEMPORAL-BASED METHOD

Iterations	SSC (g L^{-1})	Sediment retained (g) (= SSC \times 8.68 L)
0	0.161	1.398
1	0.160	1.388
2	0.159	1.378
2.07	0.158	$(1.368 \times 0.07) = 0.096$

Total sediment retained = 4.26 g

Therefore:

Anticipated sediment retention by sampler = 4.26 g

EFFICIENCY OF SAMPLER USING TEMPORAL-BASED METHOD**Grab sample-based calculations (for Kao 1)**

Iterations	SSC (g L⁻¹)	Sediment retained (g) (= SSC x 8.68 L)
0	0.1411	1.225
1	0.1335	1.159
2	0.1335	1.159
2.07	0.1335	(1.159 x 0.07) = 0.0811

Anticipated sediment retention by (Kao 1) sampler = 3.624 g

Grab sample-based calculations (for Kao 2)

Iterations	SSC (g L⁻¹)	Sediment retained (g) (= SSC x 8.68 L)
0	0.1328	1.153
1	0.1368	1.187
2	0.1368	1.187
2.07	0.1368	(1.187 x 0.07) = 0.0831

Anticipated sediment retention by (Kao 2) sampler = 3.61 g

Grab sample-based calculations (for Kao 3)

Iterations	SSC (g L⁻¹)	Sediment retained (g) (= SSC x 8.68 L)
0	0.137	1.189
1	0.1363	1.183
2	0.1363	1.183
2.07	0.1363	(1.183 x 0.07) = 0.0828
Anticipated sediment retention by (Kao 3) sampler = 3.638 g		

Grab sample-based calculations (for Riv 1)

Iterations	SSC (g L⁻¹)	Sediment retained (g) (= SSC x 8.68 L)
0	0.0665	0.577
1	0.0253	0.22
2	0.0253	0.22
2.07	0.0253	(0.22 x 0.07) = 0.0154
Anticipated sediment retention by (Riv 1) sampler = 1.032 g		

Grab sample-based calculations (for Riv 2)

Iterations	SSC (g L⁻¹)	Sediment retained (g) (= SSC x 8.68 L)
0	0.0842	0.731
1	0.0178	0.155
2	0.0178	0.155
2.07	0.0178	(0.155 x 0.07) = 0.0108
Anticipated sediment retention by (Riv 2) sampler = 1.052 g		

Grab sample-based calculations (for Riv 3)

Iterations	SSC (g L⁻¹)	Sediment retained (g) (= SSC x 8.68 L)
0	0.0726	0.63
1	0.0181	0.157
2	0.0181	0.157
2.07	0.0181	(0.157 x 0.07) = 0.011
Anticipated sediment retention by (Riv 3) sampler = 0.955 g		

Table A1.1 Phillips sampler efficiency results using temporal-based and grab sample-based calculation methods. Note that sample efficiency increases marginally for Kao trials (+4.2% - 6.5%) compared to Riv trials (+47.7% - 69.1%) between temporal and grab sample calculation methods.

Sediment source	Total sediment retained (g)	Anticipated sediment retained (grab sam- ple) (g)	Anticipated sediment retained (temporal) (g)	Sampler efficiency (grab sample) (%)	Sampler efficiency (temporal) (%)
Kao 1	1.0337	3.624	4.26	28.5	24.3
Kao 2	1.5352	3.61	4.26	42.5	36
Kao 3	1.5769	3.638	4.26	43.4	37
Riv 1	0.6505	1.032	4.26	63	15.3
Riv 2	0.9003	1.052	4.26	85.6	21.1
Riv 3	0.8513	0.955	4.26	89.1	20

APPENDIX A2: Tabulated rank sum test results

Table A2.1 Mann-Whitney *U*-test results for Forestry sites vs. Control sites

Signature property	<i>U</i> -value	<i>P</i> -value	Signature property	<i>U</i> -value	<i>P</i> -value
Al	59	0.345	Hg	103	0.168
Sb*	132	0.003	Mo	109	0.084
As	84	0.727	Ni	78	1.000
Ba	109	0.085	P	96	0.317
Be	82	0.809	K	74	0.893
Bi	107	0.100	Se	91	0.459
Cd	81	0.869	Si	99	0.244
Ca	109	0.085	Ag	106	0.118
Cr	81	0.870	Na	89	0.536
Co	62	0.427	Sr	104	0.153
Cu	76	0.979	Sn	91	0.460
Fe	92	0.434	Ti*	124	0.009
Pb	94	0.373	U	110	0.075
Li	54	0.208	V	107	0.107
Mg	77	1.000	Zn	103	0.166
Mn*	18	0.001	Zr*	116	0.033

* Significant at $P=0.05$ **Table A2.2** Mann-Whitney *U*-test results for Agriculture vs. Control

Signature property	<i>U</i> -value	<i>P</i> -value	Signature property	<i>U</i> -value	<i>P</i> -value
Al	66	0.294	Hg	74	0.503
Sb	113	0.226	Mo*	153	0.001
As*	129	0.044	Ni	95	0.767
Ba	121	0.110	P	80	0.716
Be	82	0.790	K	108	0.342
Bi*	142	0.008	Se	81	0.748
Cd	114	0.217	Si	88	1.000
Ca	73	0.481	Ag	79	0.656
Cr	75	0.544	Na	78	0.645
Co	85	0.882	Sr	81	0.748
Cu	71	0.422	Sn	90	0.961
Fe	90	0.942	Ti	88	1.000
Pb	109	0.316	U	95	0.748
Li	102	0.505	V	92	0.882
Mg	116	0.178	Zn	95	0.753
Mn	61	0.195	Zr	74	0.505

* Significant at $P=0.05$

Table A2.3 Mann-Whitney *U*-test results for Mining vs. Control

Signature property	<i>U</i> -value	<i>P</i> -value	Signature property	<i>U</i> -value	<i>P</i> -value
Al*	28	0.004	Hg	112	0.129
Sb	70	0.516	Mo*	127	0.022
As	110	0.164	Ni*	34	0.012
Ba	47	0.069	P	93	0.610
Be	52	0.121	K*	44	0.047
Bi	53	0.123	Se	107	0.211
Cd	72	0.585	Si	66	0.413
Ca	95	0.540	Ag	54	0.137
Cr*	17	0.000	Na*	36	0.015
Co*	33	0.010	Sr*	36	0.016
Cu	100	0.384	Sn	54	0.148
Fe*	24	0.002	Ti*	8	0.000
Pb	46	0.061	U	70	0.516
Li	47	0.069	V*	9	0.000
Mg*	38	0.020	Zn	72	0.610
Mn	65	0.384	Zr*	11	0.000

* Significant at $P < 0.05$ **Table A2.4** Resulting Kruskal-Wallis *H*-test values when applied to the intra-land use candidate signature property dataset for forestry (i.e. F1 vs. F2 vs. F3)

Signature property	<i>H</i> -value	<i>P</i> -value	Signature property	<i>H</i> -value	<i>P</i> -value
Al*	7.539	0.023	Hg	0.658	0.720
Sb	0.630	0.730	Mo	0.716	0.699
As	0.524	0.770	Ni	0.024	0.988
Ba*	7.357	0.025	P	0.195	0.907
Be*	8.095	0.018	K	2.000	0.368
Bi	0.757	0.685	Se	2.756	0.252
Cd	1.320	0.517	Si	2.367	0.306
Ca	3.800	0.150	Ag	0.666	0.717
Cr	1.624	0.444	Na	0.457	0.796
Co	0.067	0.967	Sr	2.657	0.265
Cu	0.214	0.898	Sn	1.181	0.554
Fe	1.014	0.602	Ti	0.329	0.849
Pb	0.595	0.743	U*	9.365	0.009
Li	4.381	0.112	V	2.214	0.331
Mg	2.081	0.353	Zn*	8.593	0.014
Mn	0.995	0.608	Zr	2.995	0.224

 $\chi^2_{0.05, 2} = 5.991$

* Signature properties with significant variability

Table A2.5 Resulting Kruskal-Wallis *H*-test values when applied to the intra-land use candidate signature property dataset for agriculture (i.e. A1 vs. A2 vs. A3)

Signature property	<i>H</i> -value	<i>P</i> -value	Signature property	<i>H</i> -value	<i>P</i> -value
Al*	10.741	0.005	Hg*	6.627	0.036
Sb	4.254	0.119	Mo*	6.859	0.032
As*	9.122	0.011	Ni*	9.706	0.008
Ba*	9.934	0.007	P*	10.110	0.006
Be*	7.635	0.022	K*	9.912	0.007
Bi*	8.098	0.018	Se*	10.177	0.006
Cd	1.358	0.507	Si*	7.371	0.025
Ca*	11.663	0.003	Ag*	7.009	0.030
Cr*	9.771	0.008	Na*	10.110	0.006
Co*	9.852	0.007	Sr*	10.110	0.006
Cu*	8.482	0.014	Sn	4.887	0.087
Fe*	10.110	0.006	Ti*	9.771	0.008
Pb*	9.122	0.011	U*	10.499	0.005
Li*	8.553	0.014	V*	10.499	0.005
Mg*	10.741	0.005	Zn*	8.593	0.014
Mn*	8.946	0.011	Zr*	10.514	0.005

 $\chi^2_{0.05, 2} = 5.991$

* Signature properties with significant variability

Table A2.6 Resulting Kruskal-Wallis *H*-test values when applied to the intra-land use candidate signature property dataset for mining (i.e. M1 vs. M2 vs. M3)

Signature property	<i>H</i> -value	<i>P</i> -value	Signature property	<i>H</i> -value	<i>P</i> -value
Al*	7.817	0.020	Hg*	9.966	0.007
Sb*	6.153	0.046	Mo*	11.567	0.003
As*	6.150	0.046	Ni*	6.558	0.038
Ba*	11.125	0.004	P*	9.483	0.009
Be*	6.144	0.046	K*	9.567	0.008
Bi*	7.549	0.023	Se*	9.017	0.011
Cd*	8.723	0.013	Si*	8.100	0.017
Ca*	6.267	0.044	Ag*	9.939	0.007
Cr*	10.392	0.006	Na*	10.350	0.006
Co	4.083	0.130	Sr*	8.458	0.015
Cu*	11.017	0.004	Sn*	9.525	0.009
Fe	5.600	0.061	Ti	3.725	0.155
Pb*	12.150	0.002	U*	9.150	0.010
Li*	8.100	0.017	V	2.500	0.287
Mg*	6.525	0.038	Zn*	10.750	0.005
Mn*	9.225	0.010	Zr	0.725	0.696

 $\chi^2_{0.05, 2} = 5.991$

* Signature properties with significant variability

APPENDIX A3: Suspended and bed sediment-associate contaminant concentrations

Since limited monthly samples were collected for bed sediment (i.e. 2-3 samples per site with several gaps in the data set), there was insufficient resolution to determine any temporal trends, much less make meaningful comparisons to suspended sediment results. However, combined values for each land use were useful for spatial inter-land use variation analysis. As a reminder, in section 3.3.2 it was identified that As and Se for mining, and Mn and Se for agriculture, exceeded upper SQG thresholds for bed sediments. Figure A3.1 compares mean suspended and bed sediment-associated concentrations for the five COI. In most cases, bed sediment values were similar or lower than suspended sediment values. Results for two COI proved to be exceptions, as bed sediment levels were elevated for mining for As, and across all land use types for Se. Evidently, most Se was predominantly in storage in QRB bed sediment and subsequently underwent less resuspension and transport associated with the suspended load than other COI. The reasons for this were not openly apparent, especially since elevated bed sediment concentrations were not exclusive to a given land use type, making connections between specific site characteristics and contaminant storage uncertain.

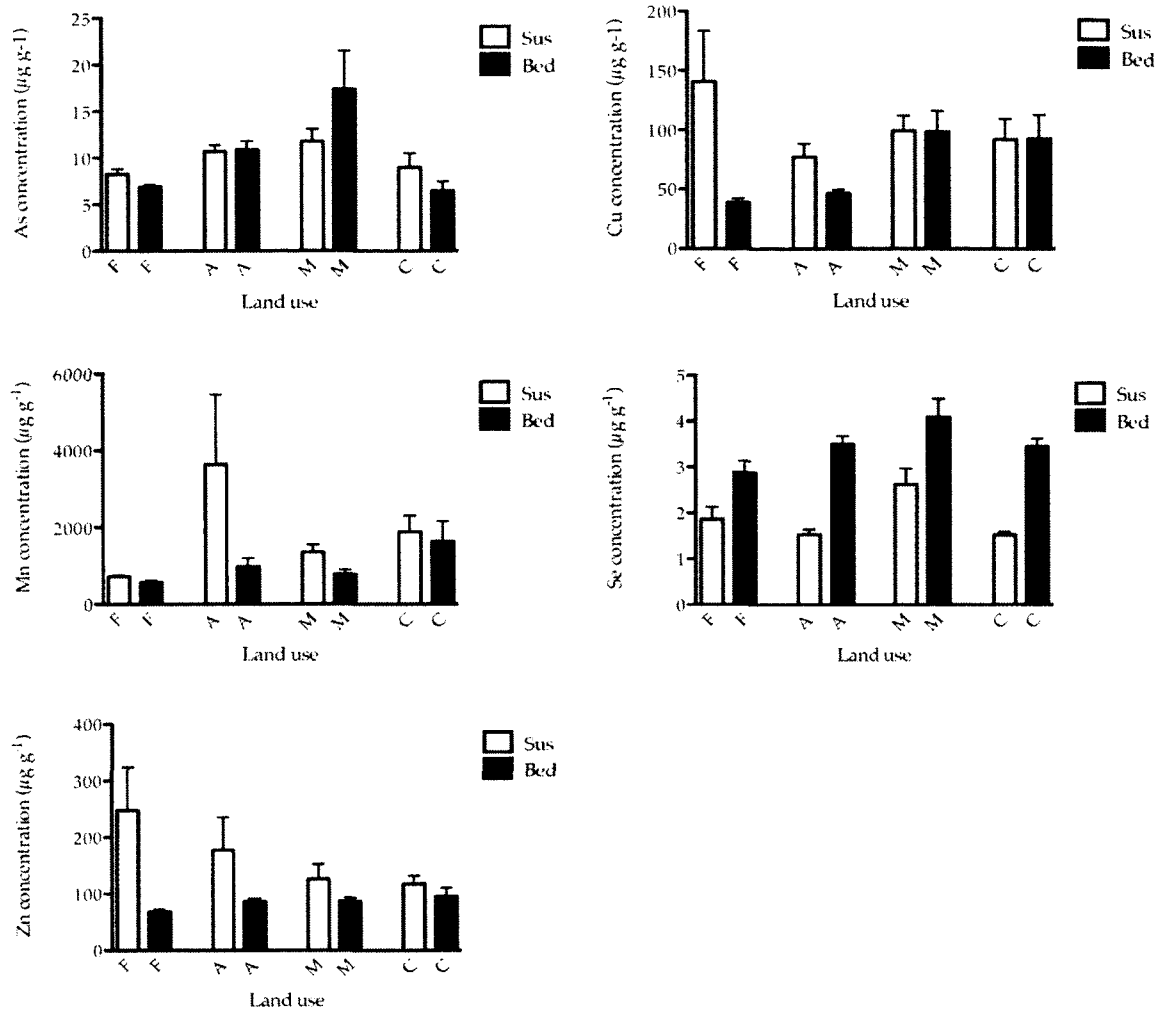


Fig. A3.1 Comparison of mean suspended (Sus) and bed sediment concentrations for contaminants of interest (As, Cu, Mn, Se, and Zn) for each land use type. All values are corrected for differences in particle size.

Other notable differences included elevated Cu and Zn concentrations for forestry, and Mn for agriculture. These differences suggested that pulses of contaminant-laden suspended sediment load were transported in each respective stream, but were not stored in high concentrations in the site-associated bed load. This may reflect preferential deposition of the coarser fraction of the sediment load on the channel bed, and/or chemical transformations between the bed sediment and the overlying water column.

APPENDIX A4: R scripts for creating a composite fingerprint signature

Kruskal-Wallis *H*-test (e.g. for Zr)

```
Zr=read.csv("data_location.csv",header=T)
```

```
Zr.kw = kruskal.test(Zr)
```

```
Zr.kw
```

Stepwise discriminant function analysis

```
> errorRate <- function(object, ...) {
+   if(!require(MASS)) stop("you need the MASS package installed")
+   UseMethod("errorRate")
+ }
> errorRate.lda <- function(object, data = eval.parent(object$call$data),
+   type = "plug-in") {
+   pred <- predict(object, data, type = type)$class
+   actu <- eval(formula(object)[[2]], data)
+   conf <- table(pred, actu)
+   1 - sum(diag(conf))/sum(conf)
+ }
>
> eRates <- function(object, data = eval.parent(object$call$data),
+   type = "plug-in") {
+   f <- formula(object)
+   r <- data.frame(formula = deparse(f[[3]]),
+     Error = errorRate(object, data,
+       type = type))
+   while(length(f[[3]]) > 1) {
+     f[[3]] <- f[[3]][[2]]
+     object$call$formula <- f
+     object <- update(object, data = data)
+     r <- rbind(data.frame(formula = deparse(f[[3]]),
+       Error = errorRate(object, data,
+         type = type)),
+       r)
+   }
+   r
+ }
> require(klaR)
> QRBdfa=read.csv("/Users/tysmith/Documents/Thesis (MSc)/Sed da-
ta/Sus/Cor/DFA/QRBdfa.csv",header=T)
> gw_obj <- greedy.wilks(LANDUSE ~ ., data = QRBdfa, niveau = 0.1) ## NB large 'niveau'
> require(MASS)
> fit <- do.call(lda, list(formula = formula(gw_obj),
+   data = quote(QRBdfa)))
> errorRate(fit)
[1] 0
> eRates(fit)
      formula      Error
1          V 0.41666667
2        V + Mg 0.16666667
3      V + Mg + Al 0.04166667
4    V + Mg + Al + Zr 0.00000000
5  V + Mg + Al + Zr + Co 0.00000000
6 V + Mg + Al + Zr + Co + Mo 0.00000000
7 V + Mg + Al + Zr + Co + Mo + Bi 0.00000000
8 V + Mg + Al + Zr + Co + Mo + Bi + Fe 0.00000000
```